

Short communication

Combined experimental and theoretical study of deprotonated ferrocene: Anion photoelectron spectroscopy and density functional calculations

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ABSTRACT

This report presents the anion photoelectron spectrum of the mass-selected, dehydrogenated ferrocene anion (deprotonated neutral ferrocene), $(\text{FC-H})^-$ as well as density functional calculations relating to $(\text{FC-H})^-$ and associated species. The measured vertical detachment energy (VDE) was found to be 1.79 eV, which compares very well with our calculated VDE value of 1.77 eV.

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1. Introduction

Ferrocene, discovered in 1951 [1], is widely considered to have launched the field of organometallic chemistry, and has since remained a molecule of interest due to its unique chemical properties [2]. A growing body of research has demonstrated that ferrocene derivatives have a variety of applications in such diverse fields as organic synthesis, material science, polymer chemistry [3], and medicine [4]. Ferrocene has also been used prevalently as an electrochemical standard [5]. These numerous applications have motivated a range of experimental [6,7] and theoretical [8–10] studies on its electronic structure.

Despite the interest in ferrocene and ferrocene derivatives, relatively few studies deal with the electrophilic properties of ferrocene. The parent anion of ferrocene is unstable in the gas phase. Two separate electron transmission spectroscopic studies examined the energies of short-lived anions of ferrocene in the gas phase [11,12]. In the condensed phase, an electrochemical study found the parent ferrocene anion to form but to persist for only a few minutes in solution [13]. When ferrocene is subjected to free electrons, it undergoes dissociative electron attachment, producing an anionic

fragment that can be regarded either as the dehydrogenated ferrocene anion or a deprotonated neutral ferrocene molecule.

In this study, we generated deprotonated ferrocene, $(\text{FC-H})^-$ and studied it via gas-phase, negative ion photoelectron spectroscopy. We measured its vertical detachment energy (VDE) experimentally, and found it to be in excellent agreement with the theoretical value we calculated using density functional theory (DFT). We also showed, via DFT calculations, ferrocene (FC) to have a negative adiabatic electron affinity, explaining why the ferrocene parent anion $(\text{FC})^-$ was not observed experimentally in the gas phase. To develop a clearer picture of this process, we also calculated the relative enthalpies of several neutral and anionic ferrocene species.

2. Experimental methods

The experimental portion of this work consisted of generating the $(\text{FC-H})^-$ anionic fragments by dissociative electron attachment of ferrocene, identifying them by mass spectrometry, mass selecting $(\text{FC-H})^-$, and measuring the anion photoelectron spectrum. This anion was produced by the co-expansion of ferrocene vapor and argon at a total pressure of 1–4 atm through a 20 μm nozzle into a high vacuum. Low partial pressures of ferrocene vapor were produced by gently heating (50 °C) powdered ferrocene in the stagnation chamber of the molecular beam source. The resultant jet was intercepted as it left the nozzle by a stream of electrons produced by a negatively biased, hot thoriated iridium filament. This resulted in the formation of a micro-plasma, which itself was confined by

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an axial magnetic field. The resulting anions were then extracted, formed into a beam, focused, and mass analyzed by a 90° sector magnet. The ion of interest was then selected by tuning the magnetic field and sent into an ion-laser interaction region, where it was irradiated with photons from an argon ion laser operating intracavity at 488 nm (2.540 eV). The resulting photodetached electrons were next energy-analyzed with a hemispherical electron energy analyzer and counted. The photodetachment process is governed by the energy-conserving relationship $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. The experimental apparatus has been described in detail elsewhere [14].

3. Theoretical methods

The Gaussian 09 software package [15] was used to predict physical properties of the ferrocene molecule, including ionization energy, optimized geometry and optimized state enthalpy. Since it has been shown previously to yield accurate results for transition metal complexes, the CAM-B3LYP [16] density functional was used for all calculations reported in this study [17–19]. The 6-311+G(2d,p) basis set was used to calculate optimized geometry and vibrational frequency calculations. The 6-31+G(d,p) basis set was used to scan the C-H potential energy surface. Geometry optimization and vibrational frequency calculations were performed on all five structures studied in order to determine optimal geometries and spin multiplicities. Where applicable, vibrational analysis of optimized structures were performed to generate thermochemical energies and to confirm the molecule was indeed at a minimum on the potential energy surface. In order to validate the accuracy of this method, the ionization potential of neutral ferrocene was calculated. The calculated value of 7.250 eV was in good agreement with previously published values (6.9 eV [20], 6.90 eV [21], 7.05 eV [22], and 7.15 eV [23]).

4. Results and discussion

The dehydrogenated ferrocene anion, $(\text{Fc-H})^-$, dominated the mass spectrum due to ferrocene having undergone dissociative electron attachment to form $(\text{Fc-H})^-$



The electrons for this process came from the thermionic emission of a hot thorium/iridium filament in the ion source. While the bias of the filament produces electrons with tens of electron volts of energy, many much lower energy electrons are also produced once the primary electrons interact with argon in the gas expansion. The photoelectron spectrum of $(\text{Fc-H})^-$ is presented in Fig. 1.

The anion photoelectron spectrum of $(\text{Fc-H})^-$ contains a broad peak centered at 1.79 eV (based on a Gaussian fit). This value is the vertical detachment energy (VDE) of $(\text{Fc-H})^-$. The theoretical results are in excellent agreement with this result. Our predicted value of 1.77 eV is within 1% of the recorded value of 1.79 eV. The agreement between theory and experiment for this quantity validates the computational methods used in this study and promotes confidence in the values for other quantities calculated herein. The electron affinity of the dehydrogenated ferrocene molecule was calculated to be 1.44 eV (Table 1). Although the spectral envelope in Fig. 1 is consistent with this value, there is no discernable peak, likely due to poor Franck–Condon overlap between the ground vibrational states of the anion and neutral species.

Our calculations also yielded additional information about the electrophilic properties of ferrocene. The relative energies of several neutral and anionic ferrocene states are tabulated in Table 1. Fig. 2 presents the energy landscape, relating these various species.

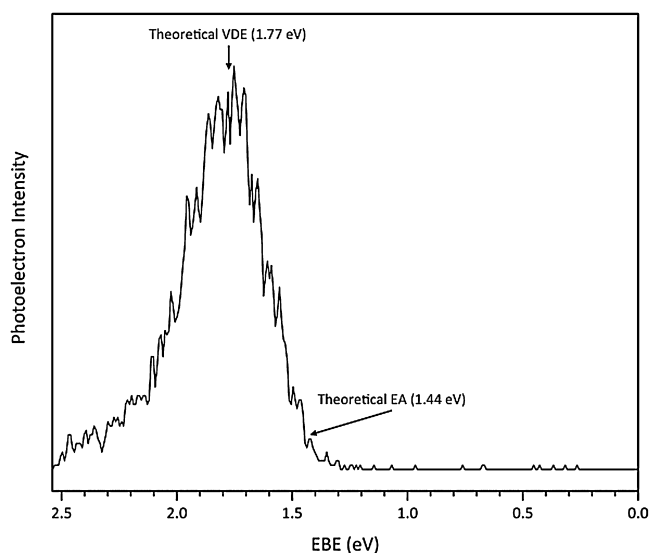


Fig. 1. Anion photoelectron spectrum of the dehydrogenated ferrocene anion, $(\text{Fc-H})^-$, measured with 2.540 eV photons.

Table 1
Energies of the relevant ferrocene species.

Name	Enthalpy (eV)	EA (eV)	VDE (eV)
Fc	0	-0.43	-
Fc+	7.20	-	-
Fc-	0.43	-	-0.44
$(\text{Fc-H})^-$	3.57	-	1.77
(Fc-H)	5.01	1.44	-

Of particular value, our calculations predicted the value of the adiabatic electron affinity of ferrocene to be -0.43 eV, consistent with it not being observed in our mass spectrum. Lastly, Fig. 3 depicts the highest occupied orbitals for both $(\text{Fc})^-$ and $(\text{Fc-H})^-$. The shape and diffuse nature of the unstable, ferrocene parent anion orbital approaches Rydberg-like character, whereas the valence orbital of the $(\text{Fc-H})^-$ fragment anion is comparatively localized, with high density on the exposed carbon atom. This brief report adds to our knowledge relating to the electrophilic properties of ferrocene and especially those of deprotonated ferrocene, $(\text{Fc-H})^-$.

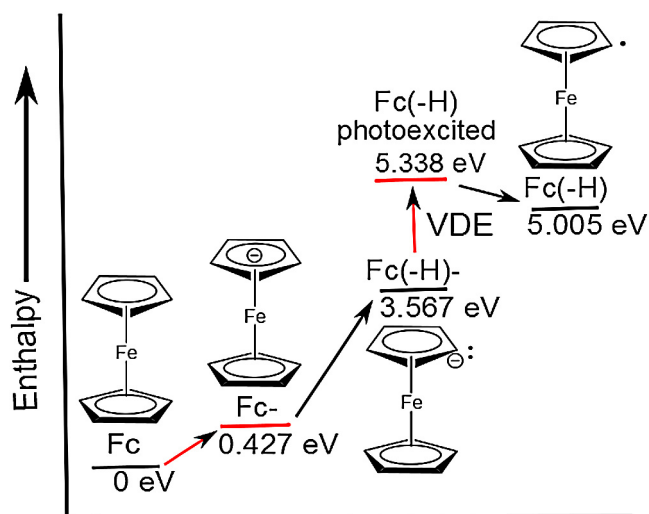


Fig. 2. Energy landscape for several neutral and anionic ferrocene species. States indicated by a red line are transient.

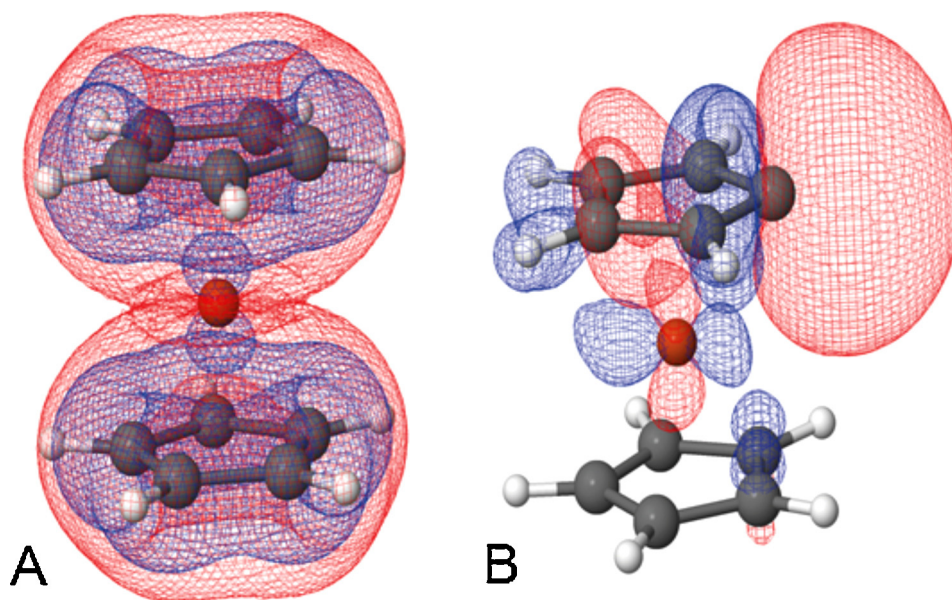


Fig. 3. (a) Singly occupied molecular orbital of $(\text{Fc})^-$ (isovalue = 0.002). (b) Highest occupied molecular orbital of $(\text{Fc-H})^-$ (isovalue = 0.02). Note that the isovalue is 10x smaller for $(\text{Fc-H})^-$ compared with $(\text{Fc})^-$. This change in scale is needed in order to properly model the diffuse SOMO of $(\text{Fc})^-$.

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