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Empirical analysis of bonding in ferrocenes

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Abstract

HeI and HeII photoelectron spectra (UPS) of 1-cyanomethyl, 1-butyryl and 1,1′-bis(dimethylsilyl)-ferrocene were measured. The nature of metal–ligand bonding was analyzed via regression analysis of UPS related experimental descriptors.

Keywords: Photoelectron spectroscopy; Ferrocenes; Bonding

1. Introduction

Ferrocene derivatives are important because of their applications in catalysis and material science [1]. Numerous studies describing their electronic structure and the nature of metal–ligand bonding have been published. Some studies used theoretical methods to investigate photoionization and photoexcitation processes in the parent ferrocene [2,3]. Others used UV photoelectron spectroscopy (UPS) to probe the nature of metal–ligand bonding in ferrocenes [4–12]. UPS was found to be a very suitable method especially when studies were performed at variable photon energies [10]. In this work, we present HeI/HeII photoelectron spectra of three ferrocenes whose spectra have not been reported previously. The ferrocenes were selected because they could be vaporized by heating without decomposition and contain ring substituents which complement those of ferrocenes studied previously (Table 2). We describe new approach to the study of bonding which relies on the correlation analysis of experimental descriptors pertinent to ligand and metal orbitals rather than on various theoretical models and calculations.

2. Experimental and computational

The sample compounds: 1-cyanomethyl-ferrocene (**1**), ferroceneacetonitrile (**2**) and 1,1′-bis(dimethylsilyl)-ferrocene (**3**) were obtained from Sigma–Aldrich and their identity checked by HPLC, melting point measurements and elemental analysis.

Photoelectron spectra were recorded on Vacuum Generators UV-G3 spectrometer and calibrated with small amounts of Xe gas which was added to the sample flow. The sample temperatures were 100, 100 and 60 °C for **1**–**3**, respectively.

DFT calculations were performed with GAUSSIAN 03 software [13] using B3LYP functional and pseudorelativistic, effective core potential basis set [14] for Fe and 6-31G* set for other atoms. In the calculations, the geometry was fully optimized at B3LYP level. Older [15] and recent [3] work have pointed out that the Koopmans approximation is inadequate for analyzing UPS of ferrocenes. Therefore, the first vertical ionization energy (E_1) was calculated by subtracting the total electron energy for the optimized, neutral molecule from the energy of the molecular ion with the same geometry. Higher vertical ionization energies were then calculated by TDDFT method which gives excitation energies for the molecular ion. The excitation energies added to IE_1 then gave approximate values for higher

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ionization energies. A similar approach was used previously [12a].

3. Results and discussion

The HeI and HeII photoelectron spectra are shown in Figs. 1–3 and the assignments are summarized in Table 1. The low energy region of the spectra (<11 eV) can be assigned by comparison with the spectra of ferrocene [5], substituted ferrocenes [6–9] and DFT calculations. As the results in Table 1 indicate the absolute differences between calculated and measured ionization energies are <0.5 eV which is comparable to Greens Functions method which is the standard method for the assignment of photoelectron spectra. The two lowest band manifolds (X–B) and (C–F) correspond to ionization from Fe3d and cyclopentadienyl (Cp) ligand orbitals, respectively. These orbitals are related to $e_2' + a_1'$ and $e_1' + e_1''$ orbitals in the parent ferrocene. The bands at 10.45 and 10.85 eV in the spectrum of **3** correspond to ionizations from Si–C σ-orbitals as can be ascertained by comparison with the spectra of silicone bridged ferrocenophanes [12a]. Band at 11.85 eV in the spectrum of **1** can be attributed to ionization from π_{CN} orbital on the basis of comparison with CH_3CN spectrum [12b]. Relative intensities of the first two band manifolds are listed in Table 1. Relative intensity of the first manifold (Fe3d ionization) increases on going from HeI to HeII excitation. Similar intensity increase has also been observed in other ferrocene derivatives and can be related to the shape resonance observed in photoionization cross-section of metallocenes at 40 eV photon energy [10]. The resonance is most apparent in the photoionization from orbitals with 3d metal character. Its presence in the continuum profile of external valence bands of metallocenes provides support for the interpretation of relative band intensity increase on going from HeI to HeII radiation as being characteristic of the initial state with metal 3d character. The measured intensity ratios of Cp vs. Fe3d manifolds (2.47) differ from

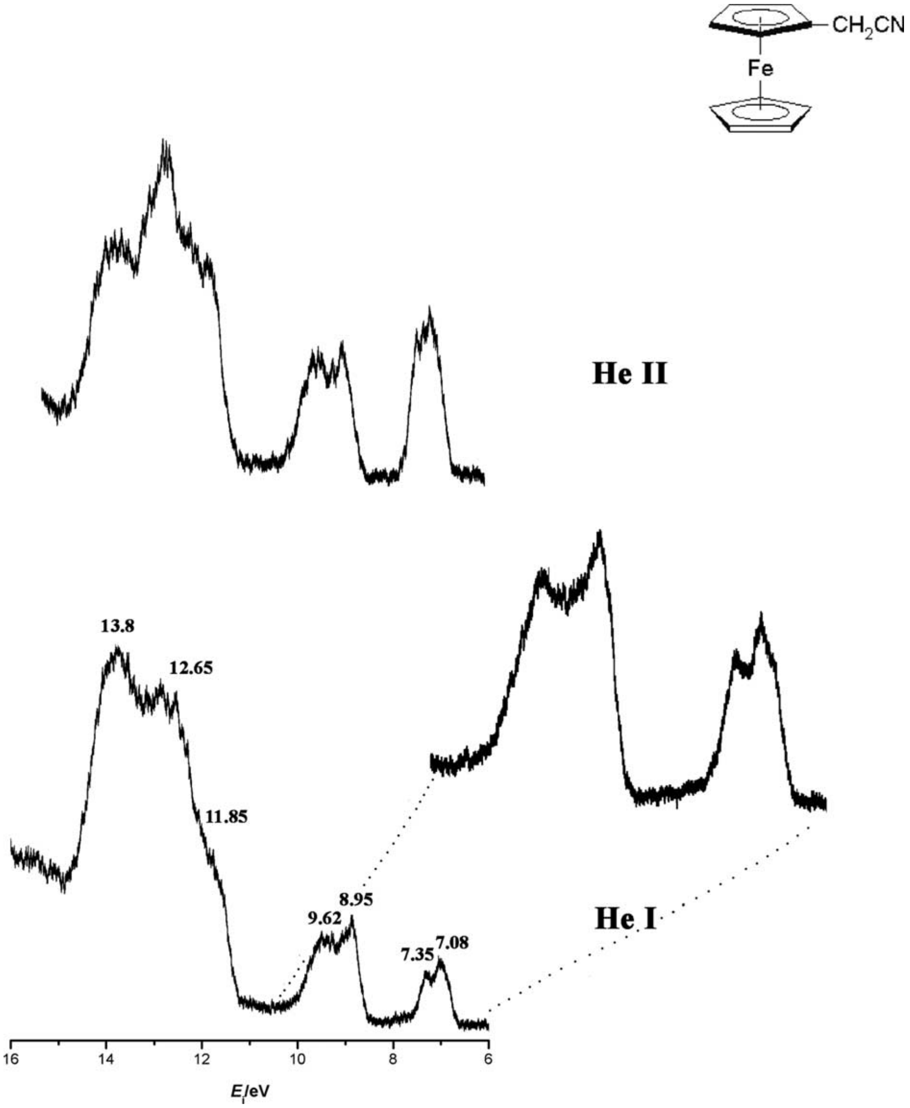

Fig. 1. HeI and HeII photoelectron spectra of **1**.