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ELECTRONIC STRUCTURE OF *trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ BY He(I) AND He(II) PHOTOELECTRON SPECTROSCOPY AND AB INITIO CALCULATIONS

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Summary

He(I) and He(II) excited photoelectron spectra of *trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ are reported. The assignment of the bands to the ionization events is based on experimental criteria as well as on the results of "ab initio" calculations. The agreement between computed and measured ionization energies appears satisfactory when the effect of the relaxation terms, especially important for ionization processes originating from predominantly metal orbitals, is taken into account.

Introduction

Many experimental and theoretical chemists are involved in research on polynuclear organometallic compounds. A primary aim of such research is the understanding of the nature of metal–metal interactions [1], which should provide insight into the mechanisms of catalytic processes. In addition to conventional spectroscopic and diffractometric techniques, at least two rela-

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tively new approaches seem to be of value in this field, namely vapour-phase photoelectron spectroscopy (PES) and the analysis of deformation density maps obtained by low-temperature diffraction methods (X-N method [2]).

Both these techniques, however, require quantum mechanical calculations if full use is to be made of their capabilities. For instance, the combined use of the PE technique and CNDO calculations recently proved effective in elucidating the electronic structure of $\text{Ru}_3(\text{CO})_{12}$ [3].

The nature of the metal-metal interaction in ligand-bridged binuclear compounds was discussed some years ago [4-6]. A crucial objective was to distinguish between direct metal-metal bonding and indirect bonding via bridging ligands.

Recently [7-10], theoretical and experimental deformation maps have shown that the hypothesis of a direct metal-metal bonding in carbonyl-bridged binuclear complexes appears inadequate.

In this paper we discuss the electronic structure of *trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ in relation both to its He(I) and He(II) excited PE spectra and "ab initio" all electron calculations.

Experimental

The sample used in the spectroscopic investigations was obtained by recrystallization and sublimation in vacuo of commercial material. Spectra were measured on a Perkin-Elmer PS-18 spectrometer modified for He(II) measurements by inclusion of a hollow cathode discharge lamp giving a high photon flux at He(II) wavelengths (Helectros Developments). Spectra were calibrated by reference to peaks due to admixed inert gases and to the He $1s^{-1}$ self ionization. Relative intensities were evaluated by fitting the spectral profiles to a series of symmetric Gaussian components. Band intensities were corrected to allow for the decrease in analyser transmittance with electron kinetic energy.

Details of the "ab initio" LCAO-MO-SCF wavefunction referred to in the discussion have been presented elsewhere [8,9]. The calculations were carried out with the ASTERIX system of programs [11]. The Gaussian basis sets used were 11, 7, 5 for Fe, 8, 4 for first row atoms, and 4 for H contracted to basis sets minimal for the inner shells and the $(n+1)s$ and $(n+1)p$ of Fe, but split for the valence shells. The geometry used in the calculations refers to the most recent X-ray determination [7] (C_{2h} point group). For comparison purposes, CNDO type calculations were also performed, using a modified treatment [12] which has proved suitable for transition metal complexes.

Results

The low ionization energy (IE) region (up to 11 eV) of the He(I) excited PE spectrum of *trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ shows four well resolved bands, labelled a, b, c and d in Figure 1. Gaussian analysis of the broad band b indicates that at least three different components contribute to its profile. Band d shows an incipient splitting in its higher IE side. The band envelope is well reproduced by two components of nearly equal width. IE's and relative intensities are reported in Table 1.

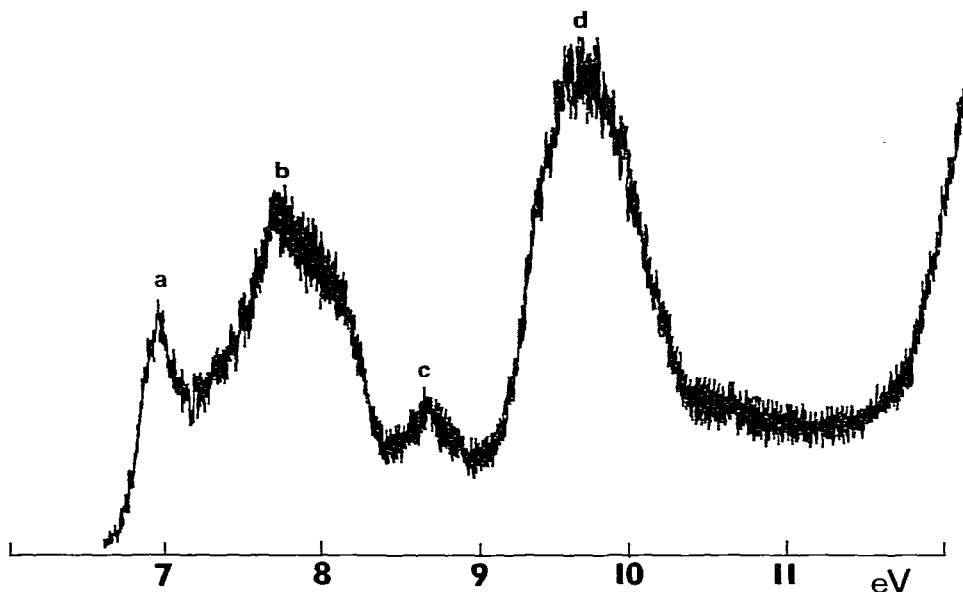


Fig. 1. He(I) PE spectrum of $trans\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (expanded scale up to 11 eV).

The spectral region that follows (up to 18 eV) consists of two very broad and ill-resolved structures (centered at 13.5 and 17.4 eV). These bands are primarily due to ionization from the metal-CO σ bonding levels, the CO 1π levels and from the C_5H_5 rings σ and inner π MO's. No detailed assignment of this region will be discussed in this paper.

Pronounced variations in relative band intensities are observed on switching from He(I) to He(II) excitation source (Figure 2 and Table 1). In particular, bands a, b and c are markedly stronger in the He(II) spectrum relative to band d.

In Table 2 the eigenvalues and the population percentage analysis of the fifteen outermost ab initio eigenvectors are listed. According to these results, the $14b_g$ HOMO is energetically quite distinct from the inner MO's, and

TABLE 1

He (I) AND He (II) PHOTOELECTRON DATA FOR $trans\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (up to 11 eV)

Band label	IE (eV)	Relative intensity	
		He (I)	He (II)
a	6.95	1.0	1.0
b	7.5	9.2	11.1
	7.76		
c	8.1	1.6	1.1
	8.68		
d	9.52	15.6	8.8
	9.9		

TABLE 2
 "AB INITIO" AND CNDO RESULTS FOR *trans*-[(η^5 -C₅H₅)Fe(CO)₂]₂

Symmetry	Eigenvalues (eV)	Population (%)		C ₅ H ₅		Dominant character ^a	CNDO eigenvalues ^b
		Fe	(CO) _b	(CO) _t	C ₅ H ₅		
14b _g	-6.954	42	47	3	7	d _{xy} + π*(CO) _b	-4.956 (14b _g)
31σ _g	-9.885	16	0	3	81	πC ₅ H ₅ MO's + d _{xy} and d _{z²}	-8.182 (30,29σ _g)
13b _g	-9.925	23	0	2	75		-8.495 (15σ _u)
16σ _u	-9.957	16	3	2	79		-8.786 (30,29σ _g)
28b _u	-9.975	18	3	1	78		-8.927 (12b _g)
27b _u	-12.657	69	21	0	10	3d metal-like MO's (d _{x²-y²} , d _{xz} , d _{yz})	-9.129 (26,27b _u)
12b _g	-13.188	70	15	4	11		-9.351 (26,27b _u)
15σ _u	-13.287	81	0	7	12		-9.622 (31σ _g)
30σ _g	-13.359	79	0	6	15		-9.638 (28b _u)
29σ _g	-13.590	73	2	2	13		-9.869 (16σ _u)
26b _u	-14.075	45	23	8	24		-9.938 (13b _g)
25b _u	-14.975	4	3	2	91	-12.648 (27,28σ _g)	
28σ _g	-15.033	3	0	1	96	-12.705 (14σ _u)	
14σ _u	-15.058	1	0	0	99	C ₅ H ₅ σ MO's	-12.714 (25b _u)
11b _g	-15.065	1	1	0	98		-12.935 (11b _g)

^a X and Y axes define the plane through iron atoms and bridging carbonyls. ^b In parentheses the corresponding "ab initio" eigenvalues.

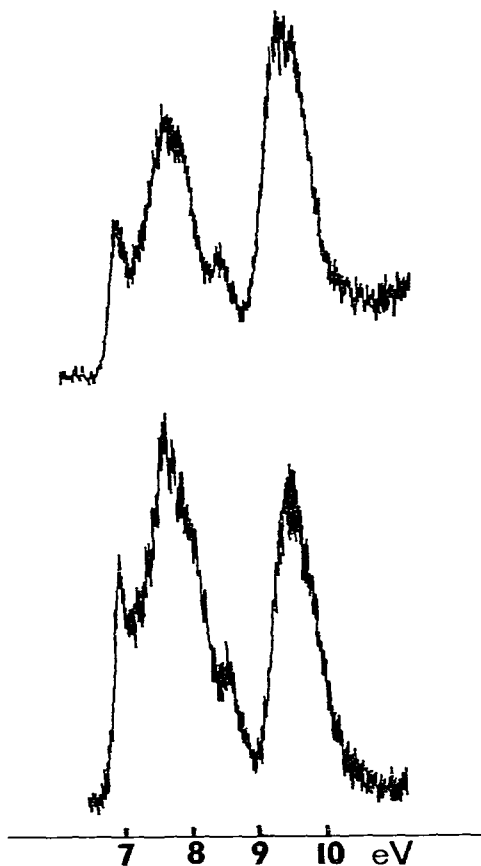


Fig. 2. He(I) (top) and He(II) (bottom) PE spectra of $trans\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$.

bridging carbonyls and iron atoms are comparably involved in this MO. The nature of this MO has been already described by one of us (M.B.) [9] as a metal-metal antibonding combination stabilized by a strong back-bonding interaction with bridging carbonyl $2\pi^*$ orbitals, thus representing a delocalized multi-centered bond. The ten subsequent inner MO's (up to $26b_u$) can be grouped into two sets according to their dominant character. The four outermost mainly represent C_5H_5 ring π MO's with some metal bonding contributions. The remaining six MO's are essentially $3d$ metal-like with some ligand contribution (among them the $26b_u$ MO possesses the most relevant ligand contribution). The following MO's (from $25b_u$) are mainly σ and π ligand levels.

For comparison purposes, CNDO eigenvalues are also reported in Table 2: the main discrepancies lie on the relative position of the C_5H_5 π and metal $3d$ levels, the latter being higher in energy according to the CNDO calculations.

Discussion

$trans\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ is diamagnetic and the 18-electron rule predicts an electron pairing between two iron atoms in the formal (d^7) oxidation state I.

Therefore 14 distinct ionizations will originate from MO's characterized by their high contribution from Fe 3d AO's. Furthermore, simply based on qualitative elementary arguments, 12 of the involved electrons should ionize from MO's maintaining 3d atom-like character (i.e. non-bonding) and the remaining two electrons should be engaged in some metal-metal interaction. The spectral region below 11 eV should also include ionizations of 8 electrons from the outermost π MO's of the C_5H_5 ligands, which correlate with the e_1'' MO of the free anion ligand in D_{5h} symmetry.

These qualitative arguments closely match the experimental pattern.

Adopting a pure experimental criterion based on the relative intensity changes (He(I) vs. He(II) exciting source), there is no doubt about assigning band d and its shoulder to C_5H_5 π MO's, and bands a, b and c to mainly Fe 3d levels. This because of the expected decrease of the cross-section ratio $\sigma(C\ 2p)/\sigma(Fe\ 3d)$ [13] on passing from He(I) to He(II) source. It is noteworthy that the He(II) relative intensity ratio * between bands a + b + c to band d (see Table 1) agrees well with the theoretical count of electrons (14 : 8 vide supra). Further on experimental grounds, the higher increase of band b in the He(II) spectrum with respect to the adjacent bands means, in terms of the Gelius model [14], that corresponding MO's have the largest Fe 3d character, whereas bands a and c must represent MO's having contributions both from Fe 3d and ligand AO's.

For the detailed assignments, we have to refer to the theoretical results shown in Table 2. It is immediately evident that within Koopmans' approximation [15] there is no matching between experimental and theoretical IE's. On the other hand, quantitative failures of Koopmans' theorem are quite common in PE spectra of transition metal complexes [16]. In particular, it has been found that the electronic relaxation which occurs upon ionization stabilizes ionic states to different extents, depending on the nature of the ionized MO. In ferrocene, a closely related molecule, Δ SCF calculations [17] pointed to a 6 eV mean relaxation energy for 3d iron-like MO's and to 0.6 eV for C_5H_5 π MO's. On empirically subtracting these values from the IE's obtained through Koopmans' theorem for our molecule, the experimental sequence (i.e. $IE\ 3d < IE\pi$) is well reproduced. It is noteworthy that CNDO results within Koopmans' approximation reproduce the sequence of the ionic states.

Problems arise in evaluating the relaxation correction term to the HOMO because of its unique features. It has been shown that the more localized the MO, the larger the relaxation energy term [18]. So it is likely that the HOMO relaxes upon ionization only to a small extent because of its delocalized nature. Thus, we propose the assignment of band a to ionization from the $14b_g$ HOMO; band b then corresponds to $27b_u$, $12b_g$, $15a_u$, $30a_g$ and $29a_g$ MO's and band c we take to represent the $26b_u$ MO. These assignments are also in keeping with the He(I)/He(II) intensity changes: bands a and c, both relating to MO's having metal contributions of ca. 45%, show a lower He(II) intensity growth than band b. Band d and its shoulder certainly represent ionization from $31a_g$, $13b_g$, $16a_u$ and $28b_u$ MO's which are the symmetric and antisymmetric pairwise

* Absolute intensity comparison between ligand and metal 3d bands is best made by using He(II) spectra, because at this wavelength 3d AO's have cross sections comparable to those of first row atoms.

TABLE 3

"AB INITIO" GROSS ATOMIC POPULATIONS FOR $trans\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$

Atomic orbital	Fe	(CO) _b		(CO) _t		C ₅ H ₅	
		C	O	C	O	5xC	5xH
<i>s</i>	6.07	3.39	3.98	3.41	3.97	17.12	4.15
<i>p</i>	12.19	2.38	4.61	2.10	4.52	14.13	
<i>d</i>	6.98						
formal charge	+0.76	+0.23	-0.59	+0.49	-0.49	-1.25	+0.85

combinations of the symmetry split components of $e''_1 \pi$ MO's of the two C₅H₅ rings. We assign the main peak to the symmetric and the shoulder to the antisymmetric combinations, the computed $a_g - b_g$ and $a_u - b_u$ splitting being lower than 0.05 eV. This evidence points to the probability that the C_{5v} local symmetry is retained as far as the Fe—C₅H₅ interaction is concerned.

Finally, it is also relevant to note the shift to higher IE of the ionizations of C₅H₅ π MO's compared to the corresponding ones in ferrocene (e_{1u} and e_{1g} ionizations at 8.8 and 9.3 eV respectively [17]). On comparing the gross atomic populations in Table 3 with the corresponding values published for ferrocene [17], we note * that a smaller overall negative charge is localized over each ring in our complex. Probably the energy difference between the π MO's of the ligand rings and the appropriate metal AO's is smaller in our case than in ferrocene because of the smaller positive charge of the iron atoms, leading to a more pronounced electron donation from C₅H₅ rings to these atoms.

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* Note that the basis sets for first row atoms adopted in the two calculations are slightly different, so that the above comparison is only valid at a qualitative level.