The Photoelectron Spectrum of Hexacarbonyl-μ-di-t-butylacetylene-di-iron: a Joint Experimental and Theoretical Study†

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The He I and He II photoelectron spectra of [Fe$_2$(CO)$_6$(Bu^{t}C$_2$Bu^t)] are reported and assigned on the basis of *ab initio* self-consistent field (SCF) and configuration interaction (CI) calculations carried out on the model system [Fe$_2$(CO)$_6$(HC$_2$H)] assuming a perfect C_s symmetry. The calculations at the SCF level lead to the possibility of a triplet ground state for the model system. However, Bu^t substitution and observed deviations from C_s symmetry, along with the pair correlation energy not accounted for in the present work, are expected to reverse this trend. The ionization energies have therefore been computed assuming a closed-shell ground state for the neutral molecule. The highest occupied molecular orbital can be described in terms of a back-donation interaction from both metal atoms to a carbonyl ligand displaying some semibridging character. The CI calculations, carried out on the ionized states using the molecular orbital set of the neutral molecule were expected to account for both the correlation effects (through two-electron excitations) and the relaxation effects (through one-electron excitations). These relaxation effects were, however, not completely accounted for, especially for localized *d* orbitals. The origin of the five bands reported between 7 and 12 eV can, however, be assigned with good confidence from the joint interpretation of the experimental and theoretical results.

This work results from a collaboration between two laboratories sharing a common interest in the multicentric metal–ligand–metal interaction in bi- and poly-nuclear complexes. On the one hand the analysis of photoelectron (p.e.) spectra has provided a considerable insight into the electronic structures of such complexes, and more specifically of acetylene-bridged binuclear systems,[1–3] and on the other hand quantum chemical calculations at the *ab initio* level have documented the concept of delocalized bonding involving both the metal atoms and the bridging ligands.[4] Up to now, semi-empirical SCF-X$_\alpha$-SW and *ab initio* calculations have contributed to the qualitative interpretation of the valence p.e. spectra of polynuclear complexes. The quantitative comparison between theory and experiment is sometimes less convincing however. Concerning more specifically *ab initio* calculations, it has been proved that a correct theoretical treatment of ionization energies must account for: (*i*) the orbital relaxation upon ionization, which can be included either from ΔSCF[5] (self-consistent field) or from configuration interaction (CI),[6] and (*ii*) the correlation effects which have been proved to be responsible either for the uniform shift toward low ionization energy (i.e.) values[2] or for the wrong ordering of some i.e. levels[6] sometimes obtained from ΔSCF calculations.

We therefore planned this joint study on [Fe$_2$(CO)$_6$(Bu^{t}C$_2$Bu^t)] in order to report the first p.e. spectrum for a complex with a formal double metal–metal bond. This complex is also remarkable because of the unusual staggered conformation of the carbonyls (Figure 1), yielding a different electronic environment for the two metals. The present work completes a series of previous studies on μ-acetylene-dimetal systems.[3] We also aimed to obtain a quantitatively reliable interpretation of this spectrum by means of *ab initio* CI techniques in order to account for both the relaxation and the correlation effects.

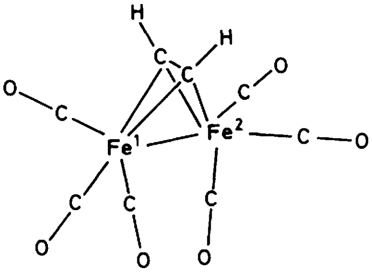

Figure 1. The [Fe$_2$(CO)$_6$(HC$_2$H)] model system

Experimental

U.v.—P.e. Spectra.—He I (21.217 eV) and He II (40.814 eV) gas-phase photoelectron spectra (Figure 2) were recorded on a Perkin-Elmer PS-18 spectrometer modified for He II measurements by inclusion of a hollow cathode discharge lamp which gives a high photon flux at He II wavelengths (Helectros Developments). A heated inlet probe system was adopted at 40—50 °C. The spectrometer was connected on-line with a Minc-23 computer (Digital Equipment) by an interface built in our laboratory. Data acquisition was carried out by several sweeps (4—6) over 500 distinct channels. Typical sweep time amounted to 5 min. The ionization energy scale was calibrated by reference to peaks due to admixed inert gases (Xe, Ar) and to the He $1s^{-1}$ self ionization. The ionization energies reported in Table 1 are the mean values over several distinct runs.

Molecular Orbital Calculations and Results.—*Ab initio* molecular orbital (m.o.) SCF calculations were carried out on

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† *Non-S.I. units employed:* eV ≈ 1.60 × 10^{-19} J, cal = 4.184 J, a.u. = 4.35 × 10^{-18}J.

Table 1. Experimental i.e. values for $[Fe_2(CO)_6(Bu^tC_2Bu^t)]$

Band label	i.e./eV
S	7.70 ± 0.04
A	8.26 ± 0.04
B	9.05 ± 0.07
C	10.24 ± 0.07
D	12.04 ± 0.06

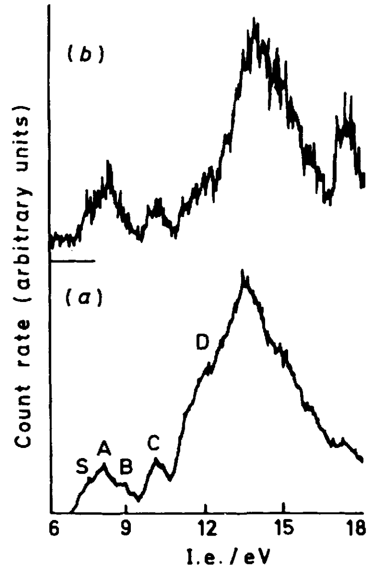


Figure 2. He I (*a*) and He II (*b*) p.e. spectra of $[Fe_2(CO)_6(Bu^tC_2Bu^t)]$

$[Fe_2(CO)_6(HC_2H)]$ (Figure 1) using the ASTERIX system of programs.[7] The geometry was deduced from the *X*-ray structure determination of Cotton *et al.*[8] carried out on $[Fe_2(CO)_6(Bu^tC_2Bu^t)]$[8] and slightly idealized in order to retain one symmetry plane (symmetry point group C_s). The Fe atoms were described by a [13,8,6] basis set obtained by adding one *p* function of exponent 0.15 and one diffuse *d* function of exponent 0.09 to the basis set optimized by Hyla-Kryspin *et al.*[9] This basis set was contracted to (5,3,3). For the first row and hydrogen atoms, respectively, we used Huzinaga's [9,5] and [4] primitive sets[10] in a split-valence contraction.

The lowest closed-shell configuration (cs1) corresponds to 50 m.o.s of A' symmetry and 25 m.o.s of A'' symmetry. The associated energy is $-3\,271.8661$ a.u. A second closed-shell configuration (cs2, 49 m.o.s of A' symmetry, 26 of A'' symmetry) was found at $-3\,271.79$ a.u. The lowest triplet state, for which both m.o.s $50A'$ and $26A''$ are singly occupied, is associated with a SCF energy of $-3\,271.8862$ a.u.

The energy difference of 13 kcal mol^{-1} in favour of the triplet state at the SCF level raises again the question of the nature of the ground state. Anderson[11] noticed the lack of any experimental report concerning the spin state of the molecule and did not exclude the possibility for a triplet ground state. The present SCF results do not provide a reliable answer to the problem since the neglect of the pair correlation energy in the closed-shell wavefunction precludes any direct comparison at the SCF level.

It should be noted however that the modelling of the real molecule $[Fe_2(CO)_6(Bu^tC_2Bu^t)]$ by $[Fe_2(CO)_6(HC_2H)]$ favours the triplet configuration. The reasons are as follows. (*i*) In order to retain the C_s symmetry in the computed model system, the acetylene ligand has been considered to be perpendicular to the metal–metal axis. It has been shown however by Hoffmann and co-workers[12] that the acetylene twist angle of 4—5° observed in the real system tends to increase the h.o.m.o.–l.u.m.o. (highest occupied and lowest unoccupied molecular orbitals respectively) gap in the cs1 configuration and therefore to stabilize this configuration with respect to the lowest triplet state. (*ii*) It is well known that the Bu^t groups in the $Bu^tC{\equiv}CBu^t$ system raise the positions of the π and π^* acetylene levels.[13,†] The substituent effect therefore contributes to raising the l.u.m.o. of the cs1 configuration through an interaction with the acetylene π^* orbital. Since the h.o.m.o. of the cs1 configuration does not indicate any significant interaction with the acetylene π orbitals, this effect also results in an increase of the h.o.m.o.–l.u.m.o. gap.

This relative stabilization of the singlet cs1 configuration by the Bu^t substituent can be related to the fact that, contrary to the equivalent complex of cobalt, $[Fe_2(CO)_6(Bu^tC_2Bu^t)]$ is the only molecule of this family of iron complexes which has ever been reported. It cannot be excluded that the replacement of Bu^t by another ligand (or by hydrogen) yields a triplet ground state for the complex, resulting in an unstable electronic structure. More accurate calculations on the singlet–triplet separation for $[Fe_2(CO)_6(RC_2R)]$ are in progress. In the present work however, the closed-shell cs1 configuration has been assumed as the ground state.

In order to compute the ionization energies accounting for both the relaxation and the correlation effects, we have taken the following procedure. (*a*) We have selected as a basis for all CI calculations the configurations constructed from a set of m.o.s corresponding neither to the singlet ground state of the neutral system, nor to any of the ionized states to be computed. Since the size of the CI expansions is relatively modest, the choice of the singlet ground state m.o.s for CI would favour the description of this state with regard to the ionized states and therefore systematically overestimate the ionization energies. All CI calculations were carried out using the molecular orbitals of the lowest triplet state. (*b*) We then performed CI expansions limited to single and double excitations for (*i*) the singlet ground state and (*ii*) each of the ionized states of interest. The ionization energy of a given ionized state will therefore correspond to the difference between the CI energies of the ionized state and of the closed-shell ground state.

Concerning the ionized states it was not technically possible to carry out a multireference CI using as root configurations the Koopmans' configurations arising from ionization of the highest valence orbitals. We rather carried out separate single reference CI expansions for each ionized configuration. In each expansion, the only root of interest is the one with maximal weight on the reference configuration.

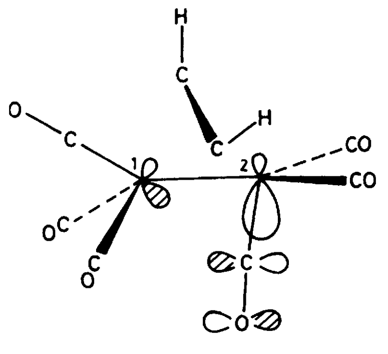
The CI expansions were carried out on an active set of 33 m.o.s (16 doubly occupied and 17 unoccupied m.o.s in the closed-shell ground-state configuration). The active m.o.s were selected according to the weight of their metal 3*d* population, so as to include in the active space most of the electrons of the 3*d* shells. A large part of the acetylene and carbonyl π and π^* electrons was also included to account for the ligand-to-metal charge transfer occurring upon ionization from localized *d* shells.

This m.o. active space generated 18 775 single and double excitations with respect to the closed-shell ground-state configuration and the associated energy was $-3\,272.1132$ a.u., yielding a correlation energy of 0.2471 a.u. For the doublet states, 20 749 configurations were generated for the A' states and 20 729 from the A'' states. The corresponding ionization energies are reported in Table 2 along with the values obtained from Koopmans' theorem.

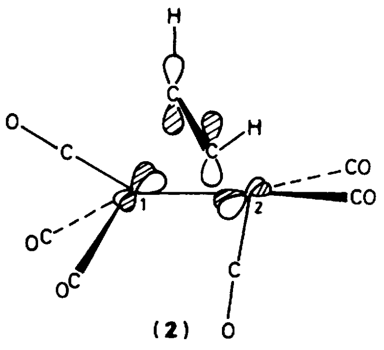
[†] Calculations on HC_2H and MeC_2Me, using the same basis set and the same bent geometry, show that the π_z^* m.o. rises from 1.96 eV in acetylene to 2.78 eV in dimethylacetylene.[14]

Table 2. *Ab initio* SCF orbital energies (eV) and charge distribution, CI level ionization energies, and proposed assignment for $[Fe_2(CO)_6(HC_2H)]$

M.o.	Koopmans theorem (eV)	Fe^1	Fe^2	HC_2H	CO	Computed i.e. (CI level)	Assignment
50*a*′	7.4	18	38	3	41	8.31	A
25*a*″	8.3	26	12	53	9	8.79	B
49*a*′	11.3	5	17	69	9	10.97	HC_2H levels (C)
48*a*′	11.6	12	24	53	11	11.70	
47*a*′	13.1	11	46	24	19	9.29	S
24*a*″	13.6	1	82	5	12	9.97	A (localized metal levels)
46*a*′	14.2	49	35	4	12		
23*a*″	14.4	85	1	1	13		
45*a*′	14.5	46	31	9	14		
44*a*′	15.5	57	17	12	14		
22*a*″	16.5	1	5	0	94		
43*a*′	17.1	2	3	0	95		
21*a*″	17.1	0	9	0	91		



(1)



(2)

Discussion

The Closed-shell Ground State.—The electronic structure of $[Fe_2(CO)_6(HC_2H)]$ has been analyzed by Anderson,[11] by Thorn and Hoffmann,[12a] and by Hoffmann *et al.*[12b] from extended Hückel theory calculations. They pointed out the presence of a low-lying empty orbital of *a*″ symmetry. The existence of a second closed-shell state at *ca.* 2 eV above the ground state and consequently, of a low-lying triplet state confirms this prediction.[†] The h.o.m.o. of the lowest closed-shell configuration labelled 50*a*′ (**1**) is stabilized by a back-bonding interaction from both Fe atoms toward the carbonyl occupying an asymmetrically bridging position between the two metals.[‡] It is noteworthy that this metal–carbonyl–metal interaction is different from the other cases of semibridging co-ordination investigated up to now,[4,15] since the h.o.m.o. representation in (**1**) does not involve a direct overlap between the metal *d* orbitals. As for the other semibridging carbonyls however, the population analysis stresses the importance of back donation. The net charge of the semibridged carbon is only +0.06 e compared to +0.36 to + 0.31 e for terminal carbonyls. The charge of oxygen is also increased, though less dramatically (−0.32 e instead of −0.27 to −0.29 e). The h.o.m.o. has 56% metal character, 38% of which comes from Fe^2 (Table 2). The 25*a*″ m.o. (**2**) represents the back donation from Fe atoms to the π* orbital of acetylene. This orbital has a large acetylene character (53%) and most of the metal weight is concentrated on Fe^1 (26% Fe^1, 12% Fe^2) in agreement with the better overlap of the Fe^1 hybrid with the acetylene π* orbital (**2**). The rotation of one $Fe(CO)_3$ unit to the staggered conformation deprives however this interaction of any metal–metal bonding character (**2**). The l.u.m.o. (26*a*″) results, in agreement with Hoffmann's calculations,[12] from the bonding interaction between the iron d_{yz} orbitals and the acetylene π_z* orbital.

As shown in (**1**) and (**2**), the formal double metal–metal bond postulated for $[Fe_2(CO)_6(HC_2H)]$ does not involve any direct coupling between the metal *d* electrons. The metal–metal interactions are effective through back-donation processes involving either the semibridging carbonyl (**1**) or the acetylene molecule (**2**). Examples of such multicentered linkages in doubly bridged binuclear systems are now rather common.[16] This work extends, however, the concept of delocalized metal–ligand–metal interaction to a new class of complexes with a formal double M–M bond.

The Photoelectron Spectrum.—Because of the well known limitations of Koopmans' theorem,[17] the orbital energies reported in Table 2 cannot be used for a direct interpretation of the p.e. spectra. The effect of relaxation, which can vary from 1—2 eV for delocalized m.o.s to 6—10 eV for localized 3*d* m.o.s is well documented.[5] Little is known, however, about the effect of correlation. From an *ab initio* study of $[Co_2(CO)_6(HC_2H)]$,[2] the correlation effects can be estimated to be 2—3 eV which represents the order of magnitude of the discrepancy between ΔSCF and experimental results.

Before attempting a correlation between theoretical and experimental ionization energies for the studied molecule, we must remind ourselves that the experimental p.e. data (Figure 2) refer to the Bu^t substituted molecule. This implies, (*i*) the presence of a broad band (D in Figure 2) to be assigned to the ionizations from σ(C–C) and σ(C–H) levels and (*ii*), more

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[†] A CI expansion including this configuration as a second reference state did not significantly modify the results presented above (total energy −3 272.1175 a.u. instead of −3 272.1132 a.u. and weight of the second root configuration less than 10%).

[‡] This carbonyl is characterized by a Fe–Fe–C angle of 81.7° and Fe–C distances of 1.80 Å with Fe^2 and 2.72 Å with Fe^1.

importantly, a shift toward lower ionization energies of the experimental values with respect to the computed ones. In this respect we must observe that π ionizations of the free alkyne change from 11.28 eV in free acetylene[2,18] to 9.2—9.4 eV in Bu^t substituted derivatives.[2] Reference to data on $[Co_2(CO)_6(RC_2R')]$ (R = R′ = alkyl) complexes indicates that the change of R and R′ produces only minor shifts (0.1—0.4 eV) in the metal-based ionizations while the alkyne ionizations are shifted by larger amounts 0.6—1.0 eV.[2]

Looking at Table 2, we notice that Koopmans' value for the i.e. associated with the h.o.m.o. (50*a*′) is 7.4 eV, *i.e.* below the first experimental peak (shoulder S at *ca.* 7.7 eV). Accounting for the substitution and relaxation effects without introducing correlation would still lower the computed i.e. value. The CI expansion yields, however, an i.e. of 8.31 eV (Table 2), 0.9 eV *above* Koopmans' value, showing that correlation is more important than relaxation in this specific case. In a similar way, the computed i.e. for the $^2A''$ state associated with the highest m.o. of *a*″ symmetry (25*a*″) is higher than its Koopmans' value (8.79 eV instead of 8.3 eV). The effects of correlation and relaxation are, therefore, approximately balanced, still with a slight excess for correlation. As indicated in Table 2, these two states are the only ones to exhibit at the CI level an i.e. higher than Koopmans' value. In particular, the six m.o.s from 47*a*′ to 44*a*′, highly localized *d* metal orbitals, are strongly relaxation dependent.

These trends must be accounted for in a tentative assignment of the experimental spectrum since it is expected that a more accurate CI treatment would produce a further shift toward higher ionization energies of the two mentioned states and a larger lower i.e. shift of the 3*d* based ionizations.[†] The spectral assignments that will be proposed also take into consideration the comparison with published p.e. data of other $[M_2(CO)_6L]$ systems [2–4,15b,19] and the experimental evidence obtained by the examination of the He II p.e. spectrum [Figure 2(*b*)]. Actually, the large intensity decrease of bands B and C compared to band A and its shoulder S strongly indicates that A and S are to be related to ionizations from localized 3*d* metal orbitals while bands B and C correspond to ionizations from delocalized m.o.s with significant contributions from the ligands.[‡]

Let us first consider the two ionizations from the π alkyne orbitals (49*a*′ and 48*a*′). No doubt exists in relating them to band C of Figure 2, mainly because of the He I—He II band intensity variation and its i.e. value. The CI computed values are in keeping with the experimental ones once the substitution effects are taken into account.

According to the reported considerations, we propose to relate band A and its shoulder S to the 3*d* metal-based ionizations, namely of the six m.o.s from 47*a*′ to 44*a*′. The splitting of band A giving rise to shoulder S could be related to the large difference in charge between Fe^1 and Fe^2 obtained from the Mulliken population analysis of the lowest closed-shell configuration (net charges of Fe^1 and Fe^2 are +0.23 and +0.14 e respectively). This difference in charge shifts the *d* orbital energies of Fe^2 to higher values with regard to the corresponding Fe^1 energies; −13.1 instead of −14.2 eV and −13.6 instead of −14.4 eV, respectively (Table 2). This computed shift is compatible with the energy difference of 0.56 eV observed between shoulder S and band A (Table 1). Shoulder S could therefore be attributed to ionization from the *d* orbitals of Fe^2 (47*a*′ and 24*a*″) whereas band A could arise from the ionization of the *d* electrons mainly localized on Fe^1 (46*a*′, 23*a*″, 45*a*′, 44*a*′).

It is highly probable that the same band envelope also contains the ionization from the 50*a*′ h.o.m.o. Although it is difficult to decide with full confidence whether this ionization contributes to shoulder S or to band A, the trend of the CI calculation with respect to Koopmans' value (Table 2) rather suggests an assignment to band A. The low intensity band B is then to be related to ionization from the 25*a*″ m.o. [represented in (**2**)] corresponding to an approximately equal weight of metal and ligand (Table 2). As already mentioned, this orbital represents a strong back-donation from metal toward the π* alkyne levels; a band of similar shape and i.e. value has been already found in the p.e. spectrum of an alkyne μ_3-η^2-co-ordinated to a trinuclear iron cluster[21] and it was assigned to the ionization from a m.o. describing a strong cluster alkyne back-donation involving the same π* alkyne level, namely that lying in the alkyne plane.

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[†] It is also well known that the relaxation contributions for *d* ionizations in symmetric binuclear complexes are better accounted for if the canonical m.o.s delocalized by the symmetry constraints are relocalized, using the Boys' method before the CI treatment is carried out.[3] In the present case, the two metal atoms are not connected by symmetry which results in a high degree of localization for most canonical m.o.s with main *d* character (Table 2).

[‡] In fact, on the basis of the Gelius model,[20] we expect a marked decrease in the cross section ratio $\sigma(C_{2p})/\sigma(Fe_{3d})$ on passing from the He I to the He II ionization source.

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