

A Green's Function Approach to the Photoelectron Spectrum of Irontetracarbonyl Dibromide: $\text{Fe}(\text{CO})_4\text{Br}_2$

MICHAEL C. BÖHM

Institut für Organische Chemie der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg, F.R.G.

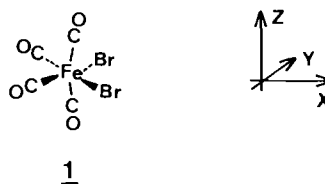
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The vertical ionization potentials of irontetracarbonyl dibromide, $\text{Fe}(\text{CO})_4\text{Br}_2$, were determined by means of the Green's function approach in the computational framework of an improved CNDO Hamiltonian. The theoretically determined sequence of the ionization events was $\text{Br}\pi < \text{Fe } 3d < \text{FeBr}\sigma$, which leads to a straightforward assignment of the measured ionization energies in the outer valence region. The ground state properties of the title compound are studied by means of the CNDO approach; the degree of metal→ligand and ligand→metal charge transfer for the various ligands (Br , CO_{ax} , CO_{eq}) of the dibromide is analyzed.

Introduction

The relative ordering of ionization potentials in transition metal polycarbonyl halides in the outer valence region has been the subject of discussion since the first published photoelectron (PE) spectra of $\text{Mn}(\text{CO})_5\text{X}$ derivatives [1]. In the case of $\text{Mn}(\text{CO})_5\text{Cl}$, contradicting assignments with respect to the ionization sequence of the Mn 3d and the chlorine lone-pair electrons have been derived on the basis of semi-empirical MO calculations [2, 3] and based on *ab initio* (minimal basis) approaches [4]. In both types of calculations the validity of Koopmans' theorem [5] has been assumed ($I_{v,j}^{\text{exp}} = I_{v,j}^{\text{K}}$, $I_{v,j}^{\text{K}} = -\epsilon_j$) where the measured vertical ionization energies, $I_{v,j}^{\text{exp}}$, are related to minus the canonical molecular orbitals energies, ϵ_j , of the electronic ground state. In the meantime various semiquantitative theoretical models for the coupling between the 3d orbitals of the transition metal center and halide lone-pairs have been presented [6–8]. On the other hand, consistent explanations of the PE spectra were derived on the basis of experimental correlation techniques (e.g. band intensities under He(I) and He(II) conditions, band shifts in series of related compounds [9]). Two typical examples where quantitative theoretical results are still missing are the PE spectra of $\text{Fe}(\text{CO})_4\text{X}_2$ ($\text{X} = \text{Br}, \text{I}$) which have been measured by Levenson and coworkers [10].

In recent publications we have shown that the ionization energies of transition metal compounds in the lower energy region can be calculated with sufficient accuracy in the framework of a perturbational approach based on the Green's function technique [11, 12]. The computational basis for the many-body approach is an improved all valence Hamiltonian of the CNDO/INDO type [13]. In this formalism electronic relaxation and correlation in the ground state and the cationic hole-states are taken into account. In the case of $\text{Fe}(\text{CO})_4\text{H}_2$ [14] and in various dihalide complexes of the general formula Cp_2TiX_2 ($\text{Cp} = \text{cyclopentadienyl}$) [15] ionization potentials have been calculated that were close to the experimental results. Therefore we found it of interest to apply the perturbational method to $\text{Fe}(\text{CO})_4\text{Br}_2$, I.



Calculations

A detailed description of the Green's function method in transition metal compounds has been given in our recent contributions [11, 12, 14–16], general reviews on this topic are summarized in ref. 17. In the following only a short outline is presented. The vertical ionization potentials derived in the one-particle Green's function approach are given by those ω values for which the matrix of the inverse Dyson equation [18] has eigenvalues equal to zero.

$$G^{-1} = (G^0)^{-1} - \Sigma(\omega) = \omega I - \epsilon - \Sigma(\omega) \quad (1)$$

G symbolizes the matrix of the Green's function and G^0 is the free counterpart. If canonical Hartree-Fock (HF) orbitals are used as one-electron basis $(G^0)^{-1}$ is given by $\omega I - \epsilon$ where I is the unit matrix of proper size and ϵ the diagonal matrix of the canonical

molecular orbitals (CMO's). $\Sigma(\omega)$ symbolizes the self-energy part which can be expanded into different orders of perturbation.

$$\Sigma(\omega) = \Sigma^{(2)}(\omega) + \dots + \Sigma^{(\infty)}(\omega) \quad (2)$$

If CMO's are employed in the perturbational approach $\Sigma^{(1)}(\omega)$ vanishes and $\Sigma^{(2)}(\omega)$ is the leading term of the infinite expansion. On the basis of our previous experience we have used a renormalized model potential for the infinite series ($\Sigma^{\text{eff}}(\omega)$) where $\Sigma^{(2)}(\omega)$ is renormalized by means of a geometric approximation. Theoretical details are discussed in ref. 14.

The computational framework for the MO calculations on *I* is the CNDO variant of a recently developed ZDO model (CNDO/INDO method) for transition metal complexes [13]. We have adopted bond-lengths and angles of the dihydride complex $\text{Fe}(\text{CO})_4\text{H}_2$ [19] while a FeBr distance of 2.26 Å has been assumed [20].

Ground State Properties

The valence orbitals of $\text{M}(\text{CO})_4\text{X}_2$ transition metal derivatives are wellknown and have been discussed in terms of a Wolfsberg-Helmholtz one-electron Hamiltonian of the Extended Hückel (EH) type [21, 22]. The CNDO results on *I* are summarized in Table I. $\text{Fe}(\text{CO})_4\text{Br}_2$ belongs to the point group C_{2v} and can be considered as a perturbed octahedron. The irreducible representations correspond to the coordinate system displayed above.

The four highest occupied MOs of *I* are ligand combinations with predominant Br lone-pair charac-

TABLE I. Valence Orbitals of $\text{Fe}(\text{CO})_4\text{Br}_2$ According to a CNDO Calculation. The Orbital Energies (ϵ_i) are given in eV. The Composition (%), the Type as well as the Irreducible Representation (Γ_i) of the MO Wave Functions are Indicated.

MO	Γ_i	MO-type	ϵ_i	%Fe	%Br	%CO
31	$7b_1$	$\text{Br}\pi/3d_{xz}$	-10.24	6.9	52.2	40.9
30	$8a_2$	$\text{Br}\pi$	-10.99	0.5	80.3	19.2
29	$12a_1$	$\text{Br}\pi/3d_{z^2}$	-11.16	7.8	51.4	40.8
28	$4b_2$	$\text{Br}\pi$	-11.58	1.0	64.9	34.1
27	$7a_2$	$\text{FeBr}\sigma/3d_{xy}$	-12.03	13.8	55.2	31.0
26	$11a_1$	$\text{FeBr}\sigma/3d_{z^2}$	-12.49	10.6	62.3	27.1
25	$6b_1$	$3d_{xz}/\text{Br}\pi$	-13.35	70.0	10.9	19.1
24	$3b_2$	$3d_{yz}$	-13.82	86.5	0.7	12.8
23	$10a_1$	$3d_{x^2-y^2}$	-14.01	86.2	0.2	13.6

ter: $7b_1$, $8a_2$, $12a_1$ and $4b_2$ (see Fig. 1). The $\text{Br}\pi$ amplitudes in $7b_1$ are destabilized by means of the $3d_{xz}$ orbital of the iron center. Important carbonyl admixtures reduce the Br contributions in $7b_1$ (52.2%). $8a_2$ at -10.99 eV is less influenced by fragment orbitals of the $\text{Fe}(\text{CO})_4$ moiety while a strong metal halide coupling is encountered in $12a_1$. The fourth member of the $\text{Br}\pi$ set ($4b_2$) is found at -11.58 eV. As shown in Table I an energy width of 1.34 eV is spanned by the four $\text{Br}\pi$ linear combinations. The following two complex orbitals are $\text{FeBr}\sigma$ MOs ($7a_2$ and $11a_1$). The center of gravity (-12.26 eV) is separated by about 1.25 eV from the center of gravity of the $\text{Br}\pi$ orbitals. It is seen that the Fe 3d contributions in $7a_2$ and $11a_1$ exceed the iron 3d admixtures in the lone-pair orbitals.

The third group of complex MOs in the outer valence region is predominantly localized at the

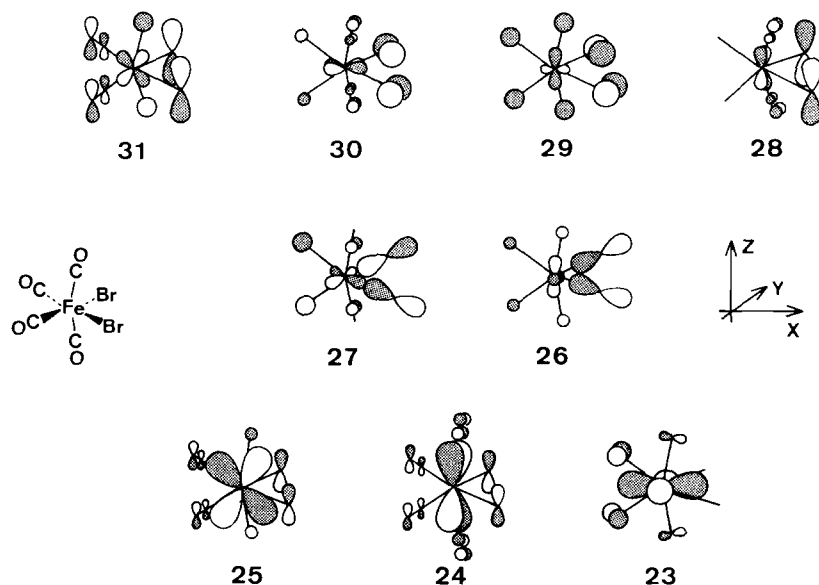


Fig. 1. Schematic representation of the highest occupied molecular orbitals of $\text{Fe}(\text{CO})_4\text{Br}_2$.

transition metal center: $6b_1$, $3b_2$ and $10a_1$. $6b_1$ at -13.35 eV is of $3d_{xz}$ type and shows the strongest interaction with the CO and the Br ligands; the 3d character amounts to 70%; this value is smaller than the Fe contribution in $3b_2$ (86.5%) and $10a_1$ (86.2%). $3b_2$ at -13.82 eV is the $3d_{yz}$ orbital while $10a_1$ (-14.01 eV) is related to $3d_{x^2-y^2}$. In the case of an unperturbed octahedron these 3d functions are combined to the triply degenerate t_{2g} set. As shown in Fig. 1 all MOs in the lower energy region show significant σ donor or π^* acceptor contributions from the four carbonyl ligands. The MO scheme of *I* suggests the classification of $\text{Fe}(\text{CO})_4\text{Br}_2$ as a d^6 complex with three occupied orbitals strongly localized at the transition metal center.

This simple classification is only a rough model, which can be rationalized on the basis of the Fe AO population and the net charges [23] summarized in Table II and on the basis of the Wiberg bond indices [24] (Table III). A Fe net charge of 0.545 is predicted while the bromine ligands are near to electroneutrality. The CO_{eq} and CO_{ax} charges indicate

TABLE II. Atomic Population at the Transition Metal Center and Net Charges of $\text{Fe}(\text{CO})_4\text{Br}_2$ According to a CNDO Calculation.

Atomic Population		
Fe	4s	0.1085
	4p _x	0.0697
	4p _y	0.0862
	4p _z	0.0370
	3d _{z²}	0.6814
	3d _{xz}	1.9387
	3d _{yz}	1.9614
	3d _{x²-y²}	1.9554
	3d _{xy}	0.6163
Net charge		
	Fe	0.5454
	Br	-0.0165
	C _{eq}	0.0919
	O _{eq}	-0.1575
	C _{ax}	0.0662
	O _{ax}	-0.2568

TABLE III. Wiberg Bond Indices of $\text{Fe}(\text{CO})_4\text{Br}_2$ According to a CNDO Calculation.

Bond	Bond index
FeBr	0.393
FeC _{ax}	0.429
FeC _{eq}	0.366
CO _{ax}	2.213
CO _{eq}	2.063

that the axial carbonyl ligands are the stronger acceptors in comparison to CO_{eq} . 0.191e are transferred to each CO_{ax} group while a net transfer of 0.066e to CO_{eq} is predicted. These charge distributions lead to the Wiberg indices collected in Table III. The FeBr index indicates significant covalent character. The calculated value of 0.393 lies between the FeC_{eq} (0.429) and the FeC_{ax} (0.366) indices.

The Calculated Ionization Energies

In the He(I) PE spectrum of *I* six maxima can be distinguished in the lower energy region [10]. The first four peaks belong to a common bandsystem with vertical ionization energies of 8.76, 9.03, 9.34 and 9.66 eV. The fifth band is very broad and has an assumed maximum of 10.63 eV. The sixth peak in the PE spectrum of *I* is found at about 11.15 eV. The center of gravity of the first four ionization events (9.20 eV) is close to the center of gravity of Br_π ionization processes in Cp_2MBr_2 complexes [25] (e.g. M = Ti 8.8 eV, M = Zr 8.90 eV). Thus peaks ①, ②, ③ and ④ have to be assigned to the complex MOs $7b_1$, $8a_2$, $12a_1$ and $4b_2$. In comparison to the Br_π IP's in CH_2Br_2 , the lone-pair ionization energies are shifted by about 1.5 eV to lower energies in the Fe tetracarbonyl complex [26].

The observed band intensities of peaks ⑤ and ⑥ suggest an assignment where ⑤ is associated with the three 'iron 3d' ionization events ($3b_2$, $10a_1$ and $6b_1$) as well as to one $\text{FeBr}\sigma$ combination while ⑥ has its origin in the remaining σ MO. The Fe3d IP's in $\text{Fe}(\text{CO})_4\text{H}_2$ are found at 9.65 eV [27] which means that the corresponding IP's are raised by about 1 eV if H is changed against Br.

The calculated ionization energies in different orders of perturbation are summarized in Table IV. The renormalized self-energy approximation leads to a straightforward assignment of the measured ionization energies. ①, ②, ③ and ④ are related to the Br_π combinations $7b_1$, $8a_2$, $12a_1$ and $4b_2$ with calculated IP's of 9.78, 10.35, 10.71 and 10.85 eV. Although the absolute values between measured and calculated ionization energies differ by about 0.8 eV, the relative gaps are predicted with high accuracy (① → ② → ③ → ④; exp: 0.27 eV → 0.31 eV → 0.32 eV; theory: 0.57 eV → 0.36 eV → 0.14 eV). The net deviations from Koopmans' theorem, $I_{v,j}^{\text{K}}$, within the Br_π set are less than 0.8 eV.

Larger reorganization effects and important renormalization contributions are found within the Fe3d MOs $3b_2$, $10a_1$ and $6b_1$. The calculated ionization energies amount to 11.19, 11.30 and 11.31 eV. In second order of perturbation $I_{v,j}^{\text{K}}$ deviations of 3.27, 3.37 and 2.53 eV are calculated, the renormalization corrections are 0.64, 0.66 and 0.49 eV which lead to final Koopmans' defects of 2.63 eV

(3b₂), 2.71 eV (10a₁) and 2.04 eV (6b₁), respectively. Once again a difference of about 0.7 eV between theory and experiment is encountered.

The high energy side of peak ⑤ is assigned to the antisymmetric FeBrσ combination (7a₂) while the sixth maximum corresponds to the symmetric 11a₁ orbital. The calculated reorganization energies of 0.49 eV (7a₂) and 0.81 eV (11a₁) are close to the Koopmans' defects derived for the Br_π combinations.

TABLE IV. Comparison between the Measured Vertical Ionization Potentials ($I_{v,j}^{\text{exp}}$, last column) of Fe(CO)₄Br₂ and Calculated Ones, Assuming the Validity of Koopmans' Theorem ($I_{v,j}^{\text{K}}$) and Using the Inverse Dyson Equation in a Second Order ($I_{v,j}^{\text{K}} + \Sigma_{jj}^{(2)}$) and in a Renormalized Approximation ($I_{v,j}^{\text{K}} + \Sigma_{jj}^{\text{eff}}$). All Values in eV.

Band	Γ_j	$I_{v,j}^{\text{K}}$	$I_{v,j}^{\text{K}} + \Sigma_{jj}^{(2)}$	$I_{v,j}^{\text{K}} + \Sigma_{jj}^{\text{eff}}$	$I_{v,j}^{\text{exp}}$
1	7b ₁	10.24	9.73	9.78	8.76
2	8a ₂	10.99	10.28	10.35	9.03
3	12a ₁	11.16	10.65	10.71	9.34
4	4b ₂	11.58	10.78	10.85	9.66
5	3b ₂	13.82	10.55	11.19	10.63 max ^a
	10a ₁	14.01	10.64	11.30	
	6b ₁	13.35	10.82	11.31	
	7a ₂	12.03	11.47	11.54	
6	11a ₁	12.49	11.57	11.68	11.16

^amax: maximum.

The computational results summarized in Table IV indicate clearly that neither Koopmans' theorem, $I_{v,j}^{\text{K}}$, nor the second order approximation to the self-energy part ($I_{v,j}^{\text{K}} + \Sigma_{jj}^{(2)}$) correspond to the measured sequence of the ionization energies. As long as $I_{v,j}^{\text{K}}$ is considered Br_π and FeBrσ are predicted on top at the three 'iron 3d' ionization processes. In the case of the second order approximation these IP's are shifted into the region of the Br_π ionization events. It is the renormalization procedure that leads to the measured IP sequence Br_π < Fe3d < FeBrσ.

Conclusions

The vertical ionization energies of Fe(CO)₄Br₂ in the outer valence region have been determined on the basis of the Green's function formalism in combination with semiempirical CNDO calculations. It has been shown that the IP's can be reproduced with sufficient accuracy. The standard error of estimate between measured and calculated ionization energies amounts to 0.15 eV, the regression coefficient is 0.964.

The sequence of the ionization energies differs from the ordering of the molecular orbitals in the

electronic ground state. In analogy to former investigations [11, 12, 14, 15], a strong correspondence between the localization properties of the orbital wave function and the calculated reorganization energies is detected.

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