

MOLECULAR  
SPECTROSCOPY

Photoelectron Spectroscopy of Molecular Systems  
and Quantum-Chemical Calculations in Terms  
of the Density Functional Theory:  
Iron  $\pi$  Complexes L–Fe(CO)<sub>3</sub>

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**Abstract**—The HeI and NeI photoelectron spectra of irontricarbonyl complexes with cyclic diene ligands— $\alpha$ -methylstyrene, orthoquinodimethane, and cyclooctatetraene—were obtained. The results of quantum-chemical calculations of the molecules of these compounds in the approximation of the density functional theory (B3LYP/6-31G\*) are presented. It is shown that this approximation describes well the excited ionic states of the  $\pi$  complexes under study. The relative ionization cross sections  $\sigma_{\pi}$  and  $\sigma_{3d}$ , which characterize the probability of removal of electrons from the molecular  $\pi$ -ligand and  $3d$ -metal orbitals, are estimated. The mechanism of the selective coordination of the Fe(CO)<sub>3</sub> groups to corresponding organic ligands is discussed. The energies of the L–Fe(CO)<sub>3</sub> chemical bond are calculated. © 2004 MAIK “Nauka/Interperiodica”.

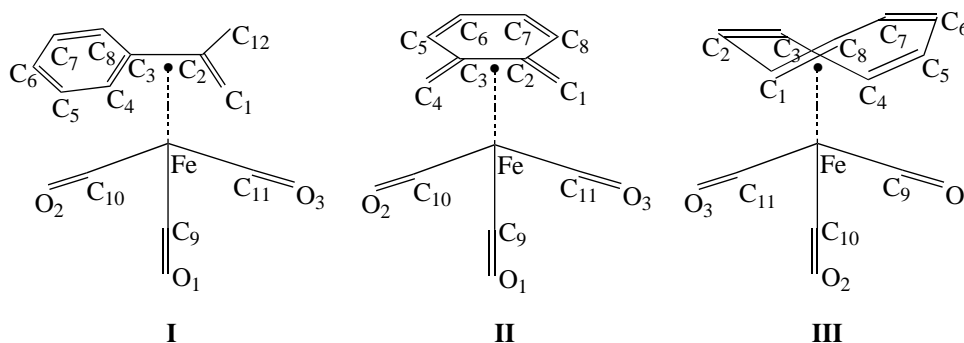
INTRODUCTION

In recent years, in connection with the development of nanotechnologies, the search for molecular systems promising for the synthesis of next-generation electronic devices, along with the study of their properties, has been actively conducted [1]. Presently known model supramolecular electronic circuits include mononuclear organometallic complexes, which show a number of interesting optical properties resulting from  $\pi$  interactions between atoms of a transition metal and organic ligands [2, 3]. The combination of different physicochemical characteristics of active components of a supramolecule leads to the appearance of qualitatively new properties, which, inter alia, are responsible for the electron transfer processes in molecular systems. It should be noted that progress in this field of science is impossible without detailed analysis of the structural and electronic characteristics of individual components of a supramolecule.

Irontricarbonyl complexes with cyclic diene ligands are  $\pi$  complexes of transition metals, convenient for detailed study of interactions between an organic molecule and a metal center. Free organic ligands are stable compounds, which have been well studied by different methods. This makes a direct comparison of the results easier and reduces the uncertainty in inferences. A characteristic feature of the structure of the complexes of ( $\alpha$ -methylstyrene)tricarbonyliron C<sub>6</sub>H<sub>5</sub>C<sub>3</sub>H<sub>5</sub>Fe(CO)<sub>3</sub> (**I**), (orthoquinodimethane)tricarbonyliron C<sub>8</sub>H<sub>8</sub>Fe(CO)<sub>3</sub> (**II**), and (cyclooctatetraene)tricarbonyliron C<sub>8</sub>H<sub>8</sub>Fe(CO)<sub>3</sub> (**III**) is selective (or frag-

mented) coordination of the Fe(CO)<sub>3</sub> group to the  $\eta^4$  fragment of an organic ligand, which has four  $\pi$  electrons (Fig. 1). The notion of selective coordination was introduced for the first time in [4]. Butadienetricarbonyliron 1,3-C<sub>4</sub>H<sub>6</sub>Fe(CO)<sub>3</sub> is a well-studied representative of the  $\eta^4$  tricarbonyliron complexes. Its electronic structure, HeI and HeII photoelectron spectra, and way of binding of butadiene with the Fe(CO)<sub>3</sub> group and the charge distribution in the complex have been the subject of many discussions [5–8]. Although the qualitative pattern of formation of chemical bonds in metal carbonyl complexes is described in the literature [9, 10], the mechanism of the  $\eta^4$  selective coordination has yet to be detailed. The available relevant publications consider mainly the interpretation of the photoelectron spectra and general aspects of the symmetry of binding [11–15]. The electron population of the molecular orbitals (MOs) of free and coordinated ligands, redistribution of the charge density, estimates of the binding energy of metal– $\pi$ -ligand bonds, and reasons for strong structural transformation of some organic molecules upon coordination to metal atoms have not been studied in detail.

The aim of this work is the interpretation of photoelectron spectra of complexes **I–III** with estimation of the energy of their ground and excited states in terms of the density functional theory and the study of the mechanism of  $\eta^4$  selective coordination of the Fe(CO)<sub>3</sub> group to cyclic diene ligands— $\alpha$ -methylstyrene (AMS), orthoquinodimethane (OQDM), and cyclooctatetraene (COT).



**Fig. 1.** Geometrical structure of the complexes of ( $\alpha$ -methylstyrene)tricarbonyliron **I** (symmetry  $C_1$ ), (orthoquinodimethane)tricarbonyliron **II** (symmetry  $C_s$ ), and (cyclooctatetraene)tricarbonyliron **III** (symmetry  $C_s$ ).

## EXPERIMENTAL

### Spectral Technique

The HeI photoelectron spectra of complexes **I** and **II** and the NeI photoelectron spectrum of complex **III** were measured with an ÉS 3201 spectrometer, whose input system was heated to 200°C. The absence of changes in the spectra during heating proved the absence of thermolysis of the compounds. On average, the energy resolution was 0.04 eV. The energy scale was calibrated with the aid of a reference gas, Xe. In all the experiments, reagent grade compounds were used.

### Photoelectron Spectra

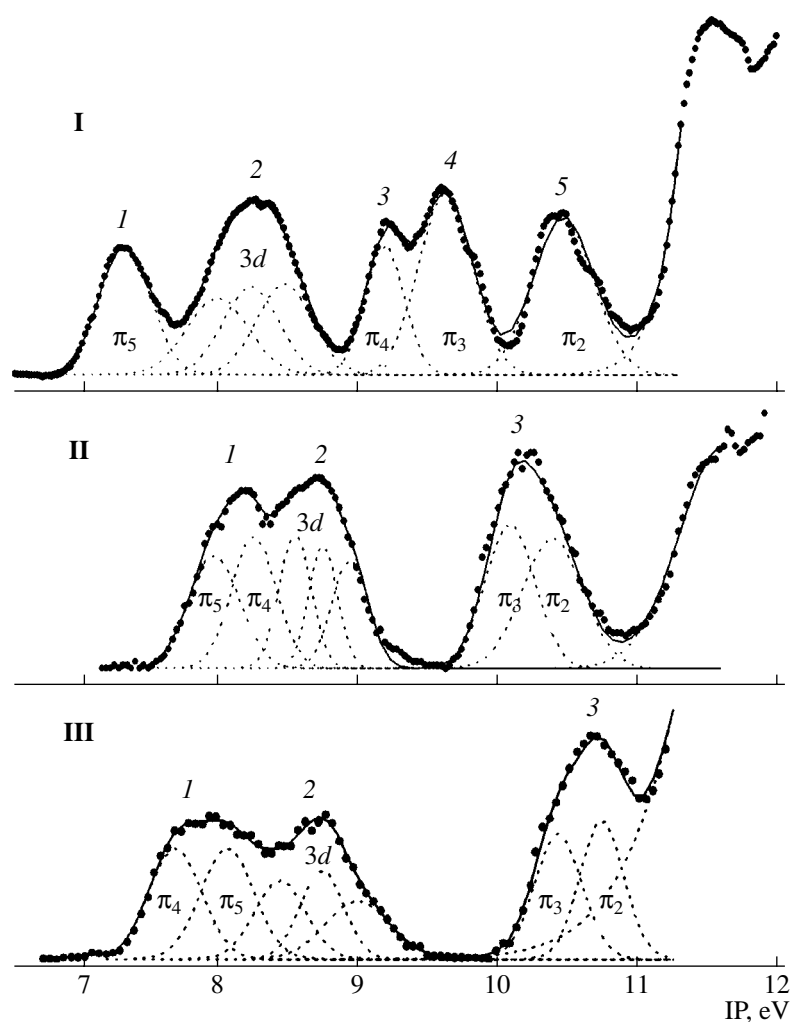
The photoelectron spectra of compounds **I–III** in the range of ionization energies 7–12 eV are presented in Fig. 2. It should be noted that the photoelectron spectra of complexes **I** and **III** were previously reported in [11, 15]. The HeI photoelectron spectrum of **II** was measured for the first time. For completeness, the photoelectron spectra of all three complexes under study are presented. As is seen, the photoelectron spectrum of

complex **I** consists of five resolved bands located at 7.30, 8.44, 9.18, 9.64, and 10.4 eV, while the spectra of complexes **II** and **III** exhibit three bands located respectively at 8.18, 8.70, and 10.25 eV and 7.80, 8.69, and 10.58 eV. On the basis of the fragments in a molecule approximation [16, 17], the complexes under study should exhibit seven resolved bands in the range 7–12 eV: four  $\pi$  bands corresponding to removal of electrons from filled  $\pi$  MOs of a coordinated ligand and three 3d bands corresponding to removal of electrons from MOs localized mostly on the iron atom. It is these valence orbitals that are involved in formation of bonding MOs of organometallic complexes. Therefore, it is obvious that the spectral bands of the complexes under study are strongly overlapped, which considerably complicates their assignment. Both the orbitals of the carbonyl groups and the  $\sigma$  orbitals of the organic ligands lie in the energy range of strongly overlapped bands, with the ionization potentials (IPs) being in the range 12–17 eV. Consequently, these bands cannot be unambiguously interpreted. Therefore, the photoelectron spectra in this range of the ionization potentials are

**Table 1.** Valence MOs of ( $\alpha$ -methylstyrene)tricarbonyliron of the symmetry  $C_1$  calculated by the density functional method (B3LYP/6-31G\*)

Band	IP, eV	IP*, eV	Energy of MO, eV	$\Gamma_j^a$	Contributions of AOs to MO, %			Character of MO
					Fe	AMS	(CO) <sub>3</sub>	
1	7.30	7.30	-5.418	66a	35.15	44.48	11.08	$\pi_5$ MO ( $\pi_5^*$ LUMO of AMS)
2	8.44	7.97	-6.655	65a	43.86	11.73	21.04	3d(Fe) MO
		8.21	-6.785	64a	39.49	23.22	17.20	3d(Fe) MO
		8.45	-7.141	63a	57.97	15.76	13.97	3d(Fe) MO
3	9.18	9.18	-7.262	62a	19.47	44.50	4.27	$\pi_4$ MO (HOMO of AMS)
4	9.64	9.62	-7.521	61a	12.21	42.40	6.96	$\pi_3$ MO (AMS)
5	10.40	10.47	-8.339	60a	5.76	48.43	2.25	$\pi_2$ MO (AMS)

Note: Vertical ionization potentials corresponding to the maxima of the Gaussian functions.



**Fig. 2.** Decomposition of the photoelectron spectra of ( $\alpha$ -methylstyrene)tricarbonyliron **I**, (orthoquinodimethane)tricarbonyliron **II**, and (cyclooctatetraene)tricarbonyliron **III** into Gaussian components. The Gaussian functions are shown by dashed lines; the approximated spectra are denoted by solid lines, and the experimentally measured spectra are indicated by dotted lines. The absorption bands of the spectra are enumerated and their spectral components are interpreted according to the calculations by the density functional method B3LYP/6-31G\*.

not shown. The vertical ionization potentials of complexes **I–III** are presented in Tables 1–3, which contain the energies of the valence MOs calculated for each complex.

To reveal the bands corresponding to individual photoionization transitions, the experimentally measured spectra of complexes **I–III** were approximated by seven Gaussian functions (Fig. 2). Restrictions on the area and half-width were imposed on the parameters of the Gaussian functions. The photoionization cross section was assumed to be dependent on the type of molecular orbital. Accordingly, the ionization cross sections for the  $\pi$  and  $3d$  orbitals should be different. The quality of the approximation curves was estimated by the  $\chi^2$  method. The resultant positions of the maxima of the Gaussian functions correspond to the energies of the excited ionic states of the molecules of complexes **I–**

**III**, and, for each complex, these positions can be brought into a unique correspondence with the calculated energies of the molecular orbitals. The values of these energies are listed in Tables 1–3.

#### Quantum-Chemical Calculations

Quantum-chemical calculations of the electronic structure of complexes **I–III** were performed in terms of the restricted method of the density functional theory with the B3LYP exchange-correlation potential in the 6-31G\* basis set with the complete optimization of the geometry of the molecules under study. For the calculations, the quantum-chemical software package GAMESS-2001 [18] was used. The calculation data was visualized using the software package HyperChem 6.02 [19].

**Table 2.** Valence MOs of (orthoquinodimethane)tricarbonyliron of the symmetry  $C_5$  calculated by the density functional method (B3LYP/6-31G\*)

Band	IP, eV	IP*, eV	Energy of MO, eV	$\Gamma_j^a$	Contributions of AOs to MO, %			Character of MO
					Fe	OQDM	(CO) <sub>3</sub>	
1	8.18	7.93	-6.221	38a'	37.78	40.22	11.18	$\pi_5$ MO ( $\pi_5^*$ LUMO OQDM)
		8.22	-6.390	24a''	12.94	48.44	2.29	$\pi_4$ MO (HOMO OQDM)
2	8.70	8.52	-6.968	37a'	50.25	12.20	19.66	3d(Fe) MO
		8.72	-7.150	23a''	41.25	16.68	18.69	3d(Fe) MO
		8.91	-7.174	36a'	75.69	7.35	16.78	3d(Fe) MO
3	10.25	10.06	-8.042	22a''	7.76	49.77	2.0	$\pi_3$ MO (OQDM)
		10.37	-8.166	35a'	7.18	46.16	3.52	$\pi_2$ MO (OQDM)

Note: Vertical ionization potentials corresponding to the maxima of the Gaussian functions.

**Table 3.** Valence MOs of (cyclooctatetraene)tricarbonyliron of the symmetry  $C_5$  calculated by the density functional method (B3LYP/6-31G\*)

Band	IP, eV	IP*, eV	Energy of MO, eV	$\Gamma_j^a$	Contributions of AOs into MO, %			Character of MO
					Fe	COT	(CO) <sub>3</sub>	
1	7.80	7.64	-5.373	24a''	10.25	52.16	4.76	$\pi_4$ MO (HOMO COT)
		8.01	-6.134	38a'	32.40	48.97	8.60	$\pi_5$ MO ( $\pi_5^*$ LUMO COT)
2	8.69	8.39	-7.003	37a'	50.93	8.21	21.88	3d(Fe) MO
		8.70	-7.382	36a'	75.46	9.56	16.61	3d(Fe) MO
		8.96	-7.398	23a''	45.84	21.41	16.69	3d(Fe) MO
3	10.58	10.42	-8.507	22a''	6.31	47.47	1.87	$\pi_3$ MO (COT)
		10.74	-8.527	35a'	5.73	45.34	1.46	$\pi_2$ MO (COT)

\* Vertical ionization potentials corresponding to the maxima of the Gaussian functions.

### The Calculation Procedure

The most appropriate expedients for describing the electronically excited states of molecules and ions are such multiconfigurational methods as the multiconfiguration self-consistent field (SCF) and configuration interaction methods. However, their application to large molecular systems, to which complexes **I–III** belong, presents difficulties. In practice, the photoelectron spectra of molecules are frequently interpreted in terms of the Koopmans' theorem in the Hartree–Fock approximation. However, the electron relaxation effects in iron  $\pi$  complexes may be as high as 8 eV [20], which makes it impossible to apply the Koopmans' theorem to the description of the photoelectron spectra of such complexes. Several calculation schemes have been developed to take into account relaxation effects, for example, the ab initio  $\Delta$ SCF method [7, 12, 13]. However, this method requires a large amount of computer time, and its application is not always warranted with respect

to the final result. Semiempirical INDO (intermediate neglect of differential overlap) calculations of the electronic structure of  $\pi$  complexes of transition metals in the ground state and in cation–hole states performed in terms of the many-particle perturbation theory based on the formalism of the Green's functions [8, 14] are also known. In comparison with the  $\Delta$ SCF calculations, such an approach better reproduces the vertical ionization potentials in the range of low energies, but it is not generally available.

Presently, quantum-chemical calculations of such molecular systems are performed in terms of the electron density functional theory [21, 22]. This method reproduces well the geometry of the ground state of a molecule; however, it is generally accepted that the Kohn–Sham orbital energies, except for the energy of the highest occupied molecular orbital (HOMO), have no definite physical meaning. At the same time, in recent theoretical publications [23, 24], attempts have

**Table 4.** Geometrical parameters of complexes **I–III** and ligands optimized by the density functional method (B3LYP/6-31G\*)

Bond lengths (Å) and valence angles (deg)	Coordinated [free] ligand		
	AMS–Fe(CO) <sub>3</sub>	OQDM–Fe(CO) <sub>3</sub>	COT–Fe(CO) <sub>3</sub>
C <sub>1</sub> –C <sub>2</sub>	1.436 [1.343]	1.450 [1.354]	1.440 [1.474]
C <sub>2</sub> –C <sub>3</sub>	1.441 [1.490]	1.444 [1.499]	1.408 [1.343]
C <sub>3</sub> –C <sub>4</sub>	1.446 [1.408]	1.450 [1.354]	1.440 [1.474]
C <sub>4</sub> –C <sub>5</sub>	1.434 [1.393]	–	1.460 [1.343]
C <sub>5</sub> –C <sub>6</sub>	1.369 [1.398]	1.373 [1.352]	1.359 [1.474]
C <sub>6</sub> –C <sub>7</sub>	1.427 [1.396]	1.420 [1.452]	1.434 [1.343]
C <sub>7</sub> –C <sub>8</sub>	1.368 [1.396]	1.373 [1.352]	1.359 [1.474]
C <sub>8</sub> –C <sub>3</sub>	1.440 [1.407]	–	–
C <sub>2</sub> –C <sub>12</sub>	1.512 [1.514]	–	–
C <sub>3</sub> –C <sub>5</sub>	–	1.431 [1.463]	–
C <sub>8</sub> –C <sub>2</sub>	–	1.431 [1.463]	–
C <sub>8</sub> –C <sub>1</sub>	–	–	1.460 [1.343]
Fe–C <sub>9</sub>	1.785	1.761	1.783
Fe–C <sub>10</sub>	1.790	1.799	1.788
Fe–C <sub>11</sub>	1.768	1.799	1.788
∠(C <sub>9</sub> –Fe–C <sub>10</sub> )	101.44	99.79	99.09
∠(C <sub>9</sub> –Fe–C <sub>11</sub> )	100.42	99.79	99.09
∠(C <sub>10</sub> –Fe–C <sub>11</sub> )	92.2	94.41	93.68
$\bar{r}$ (C–O)	1.154	1.152	1.152
Fe–C <sub>1</sub>	2.075	2.064	2.182
Fe–C <sub>2</sub>	2.062	2.159	2.061
Fe–C <sub>3</sub>	2.175	2.159	2.061
Fe–C <sub>4</sub>	2.232	2.064	2.182

been made to reveal the physical meaning of the Kohn–Sham orbital energies. In particular, in [23], it was shown for the first time that these energies can be considered as approximate vertical ionization potentials

$$\epsilon_{ks}^{(i)} = -IP^{(i)} + \Delta\epsilon_{\text{resp}}^{(i)}, \quad (1)$$

where  $\Delta\epsilon_{\text{resp}}^{(i)} = \langle \varphi_i | v_{\text{resp}} | \varphi_i \rangle$  are the matrix elements of the response potential and components of the Kohn–Sham exchange–correlation potential. Consequently, expression (1) is an analogue of the Koopmans’ theorem in the density functional theory.

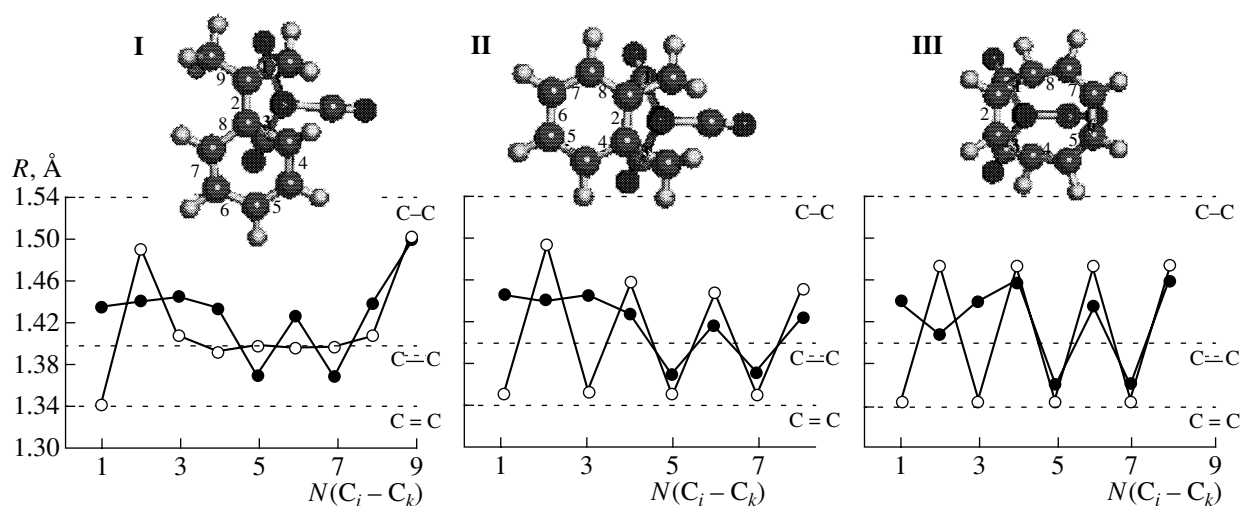
One can expect that the calculation of the ground state of complexes **I–III** by the density functional method will make it possible to obtain both an adequate geometry and the proper order of the ground states and excited ionic states of the molecules under study.

## RESULTS

### Geometry

The geometrical parameters of complexes **I–III** optimized by the density functional method, as well as those of the free organic ligands AMS, OQDM, and COT, are presented in Table 4. A comparison of these parameters with x-ray data [25–27] shows that the calculated and experimentally determined bond lengths and valence angles coincide to within 2% (here, the absolute differences of the bond lengths and valence angles are meant).

Interestingly, although the initial geometrical parameters of the free organic ligands are rather different, the bond lengths of coordinated AMS, OQDM, and COT are very similar. This is clearly illustrated in Fig. 3. If in all the ligands in their free states the lengths of the double C=C, single C–C, and aromatic carbon–



**Fig. 3.** Bond lengths of (○) free and (●) coordinated ligands AMS, OQDM, and COT. Horizontal lines correspond to the single, aromatic, and double carbon-carbon bonds. The numeration of the bonds  $N(C_i-C_k)$  is shown on the molecules.

carbon bonds are close to typical values, being respectively 1.34, 1.54, and 1.40 Å, upon coordination of the  $\text{Fe}(\text{CO})_3$  group, the bond lengths of the  $\eta^4$  fragment become partially aromatized, while the remaining part of the organic ligand acquires a diene structure.

#### *MO Analysis and Interpretation of the Photoelectron Spectra*

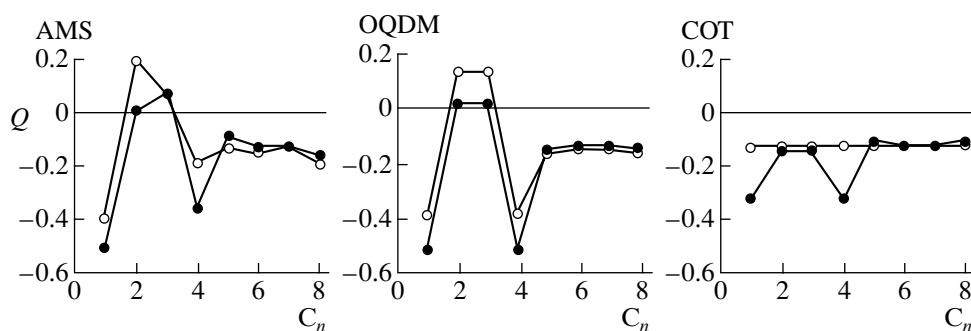
For all the complexes under study, the sequences of the valence MOs obtained by the density functional method are rather typical (Tables 1–3). A characteristic feature of the formation of chemical bonds in complexes **I–III** is the population and significant stabilization of the  $\pi_5^*$  lowest unoccupied molecular orbital (LUMO) of a ligand. This  $\pi_5$  molecular orbital (orbital 66a in **I** and orbital 38a' in **II** and **III**) has a considerable contribution (32.4–37.8%) from the atomic orbitals of iron and corresponds to band 1 in the photoelectron spectra of complexes **I–III** (Fig. 2). In the spectra of complexes **II** and **III**, band 1 also corresponds to yet another photoionization transition, which is associated with the removal of an electron from orbital 24a", having predominantly a  $\pi$ -ligand character (the HOMO of the corresponding ligand).

Band 2 in the photoelectron spectrum of complex **I** is well separated from the remaining bands and, therefore, can be readily interpreted. Indeed, the calculations show (Table 1) that the  $\pi_5$  molecular orbital is followed by a group of orbitals with energies that are close together and with large contributions (43.86, 39.49, and 57.97%, respectively) from the atomic orbitals of iron. It is logical to assume that the ionization cross sections of these 3d MOs are nearly equal and, therefore, the areas of the corresponding spectral bands are close to each other. Figure 2 illustrates the decomposition of

band 2 of the photoelectron spectrum of complex **I** into three spectral components. According to the calculations (Tables 2, 3), complexes **II** and **III** show a similar pattern: the first two  $\pi$  MOs are followed by the three orbitals that are close in energy to each other and are strongly localized on the Fe atom. For this reason, band 2 in the photoelectron spectra of these complexes should be considered as consisting of the three spectral components corresponding to the ionization from these 3d molecular orbitals. Therefore, the group of the three metal 3d MOs characteristic of all three complexes under study unambiguously corresponds to band 2, whose maximum may shift due to a positive inductive effect from the ligands. For complexes **I–III**, this shift with respect to the 3d band of the complex  $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$  amounts to  $-0.67$ ,  $-0.16$ , and  $-0.19$  eV, respectively.

The group of the metal 3d MOs is again followed by molecular orbitals of a predominantly  $\pi$ -ligand character. In complex **I**, these are orbitals 62a, 61a, and 60a (Table 1), corresponding to bands 3–5. In complexes **II** and **III** (Tables 2, 3), these are orbitals 22a" and 35a"m corresponding to band 3, decomposed into two spectral components. Such an interpretation is beyond question.

A comparison of the spectral and calculation data testifies to a good linear correlation between the Kohn-Sham energies and the vertical ionization potentials obtained from the decomposition of the photoelectron spectra of **I–III** into Gaussian components. The correlation coefficient is close to unity ( $R = 0.96$ ). Therefore, the calculation of the ground state of the molecules under study by the density functional method allows one to obtain the correct sequence of their excited ionic states.



**Fig. 4.** Charges on the carbon atoms of (○) free and (●) coordinated ligands AMS, OQDM, and COT. The numeration of the atoms is shown in Fig. 1.

#### Estimation of Relative Ionization Cross Sections

It is known that, under the assumption of the isotropy of the angular distribution of photoelectrons, the integral area of a band is proportional to the photoionization cross section  $\sigma_e$ , which characterizes the probability of removal of an electron from some molecular orbital [28, 29]. Knowing the relative areas of all the  $\pi$  and  $3d$  bands of complexes **I–III**, determined from the approximation of their photoelectron spectra, one can estimate the relative photoionization cross sections as  $\sigma_\pi/\sigma_{3d} = S_\pi/S_{3d}$ . For complexes **I–III**, these ratios are equal to  $1.58 \pm 0.05$ ,  $1.73 \pm 0.05$ , and  $1.51 \pm 0.05$ , respectively. Their average value is  $\bar{\sigma}_\pi/\bar{\sigma}_{3d} = 1.61 \pm 0.10$ , which is in excellent agreement with the ratio of the photoionization cross sections for butadienetricarbonyliron  $\sigma_\pi/\sigma_{3d} = 1.61 \pm 0.05$ . This closeness provides additional evidence for the validity of the proposed interpretation of the photoelectron spectra of complexes **I–III**.

#### Charge Distributions, Bond Populations, and Dipole Moments

The changes in the charges on the C atoms of the organic ligands due to the coordination of the  $\text{Fe}(\text{CO})_3$  groups calculated according to Mulliken are shown in Fig. 4. All the complexes under study show a noticeable change in the charges on their  $\eta^4$  fragments, especially on the terminal C atoms. The charges on other C atoms remain nearly unchanged. The total charge transfer to the AMS, OQDM, and COT ligands amounts to  $-0.20$ ,  $-0.28$ , and  $-0.27$  e, respectively. The charges on the Fe atoms of complexes **I–III** are positive, amounting to  $+0.535$ ,  $+0.559$ , and  $+0.555$  e, respectively. This agrees with ab initio calculations of unsubstituted carbonyl iron  $\text{Fe}(\text{CO})_5$  [30]. The calculated dipole moments  $\mu$  of the molecules of complexes **I–III** are equal to 3.92, 3.58, and 2.61 D, respectively. For comparison, we performed a population analysis of the natural bond orbitals [31] of complexes **I–III**, according to which the natural charges on the Fe atoms are equal to  $+0.833$ ,  $+0.842$ , and  $+0.846$  e, respectively, and the total charge transfer to the AMS, OQDM, and COT ligands amounts

**Table 5.** The Mulliken populations  $q(N_e)$  of the carbon–carbon bonds of free and coordinated ligands AMS, OQDM, and COT

Bond number (C–C) <sub>n</sub>	AMS		OQDM		COT	
	free	coordinated	free	coordinated	free	coordinated
1	0.644	0.305	0.558	0.271	0.406	0.306
2	0.371	0.348	0.431	0.424	0.660	0.386
3	0.544	0.300	0.558	0.271	0.406	0.306
4	0.551	0.365	0.467	0.509	0.660	0.366
5	0.565	0.578	0.642	0.593	0.406	0.612
6	0.572	0.477	0.455	0.518	0.660	0.474
7	0.556	0.562	0.642	0.593	0.406	0.612
8	0.534	0.455	0.467	0.509	0.660	0.366
9	0.369	0.355				

**Table 6.** Bonding energy of the L–Fe(CO)<sub>3</sub> bond of complexes **I–III** and C<sub>4</sub>H<sub>6</sub>Fe(CO)<sub>3</sub> estimated by the density functional B3LYP/6-31G\* and restricted Hartree–Fock RHF/6-31G\* + MP2 methods

Complex	$E_{\text{bond}}^{\text{DFT}}$ , eV	$E_{\text{bond}}^{\text{RHF} + \text{MP2}}$ , eV
<b>I</b>	–3.132	–3.304
<b>II</b>	–4.468	–4.221
<b>III</b>	–3.760	–3.919
C <sub>4</sub> H <sub>6</sub> Fe(CO) <sub>3</sub>	–4.062	–3.811

to –0.425, –0.516, and –0.503 e, respectively. One should not absolutize the above data in view of the known arbitrariness in the determination of charges on atoms in quantum chemistry. It is seen that the values of the charges are different, but the general trends are retained.

According to the Mulliken population analysis (Table 5), upon coordination of the ligands, the population of the double bonds of the  $\eta^4$  fragment decreases approximately twofold. Such a pattern is in complete agreement with the general understanding of the mechanism of donor–acceptor multicenter bonding. Initially, the electron density is transferred from the highest occupied  $\pi$  molecular orbital of an organic molecule to the vacant  $3d$  orbitals of the iron atom. In this way, direct donating occurs. The strengthening of a bond is achieved due to a reverse donating—a partial transfer of electrons from the occupied  $3d$  shell of a metal to the  $\pi^*$  LUMO of a ligand. The occurrence of negative charges on AMS, OQDM, and COT indicates that, in the complexes under study, the reverse donating dominates over the direct donating. The removal of an electron density from the bonding orbital and the partial population of the antibonding  $\pi$  molecular orbital of an organic ligand should lead to the weakening of the double bonds of the  $\eta^4$  fragment. This is well supported by the quantum-chemical calculations (bond population and geometrical parameters). In electronic characteristics, the  $\eta^4$  fragment is similar to free butadiene in the first excited state. It is seldom that the properties of an excited state can be studied under stationary conditions. Therefore, upon coordination of the Fe(CO)<sub>3</sub> group, a significant electronic activation of an organic ligand occurs.

#### *Estimation of the Bonding Energy of the L–Fe(CO)<sub>3</sub> Bond*

The energy of the chemical bond  $E_{A-B}$  between two fragments *A* and *B* of some molecule *AB* is commonly estimated as the difference between the total energy of this molecule and individual fragments with optimized geometrical parameters:  $E_{A-B} = E_{AB} - (E_A + E_B)$ . Table

6 presents the results of calculations of the bonding energy of the L–Fe(CO)<sub>3</sub> bond for complexes **I–III** and C<sub>4</sub>H<sub>6</sub>Fe(CO)<sub>3</sub> performed by the density functional method and by the restricted Hartree–Fock (RHF) method with regard to the electron correlation energy in the MP2 approximation (the Möller–Plesset perturbation theory of the second order).

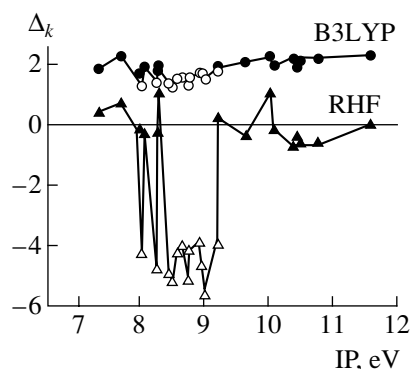
It is seen from this table that the bonding energies of the C<sub>4</sub>H<sub>6</sub>Fe(CO)<sub>3</sub> bond obtained by the density functional method are close to the bonding energies estimated by the RHF + MP2 method. For compounds **II** and **III** and C<sub>4</sub>H<sub>6</sub>Fe(CO)<sub>3</sub>, the average value of the bonding energy of the L–Fe(CO)<sub>3</sub> bond amounts to 4 eV. In the case of complex **I**, the bonding energy is markedly underestimated. We associate this with the structural characteristics of  $\alpha$ -methylstyrene, in which the C<sub>3</sub> and C<sub>4</sub> atoms of the  $\eta^4$  fragment are included into the aromatic ring and, thus, lack sufficient degrees of freedom for efficient overlapping with the  $3d$  atomic orbital of iron. The maximum overlap of the  $\pi$  system of the  $\eta^4$  fragment with the  $3d$  AO of iron is realized in complex **II**, which is reflected in the highest bonding energy of the L–Fe(CO)<sub>3</sub> bond.

## DISCUSSION

It is important to turn back to expression (1), which was presented as an analogue of the Koopmans' theorem in the density functional theory. In the Hartree–Fock theory, the deviation of the calculated energies of MOs from experimental ionization potentials is commonly called the Koopmans' defect. Its value  $\Delta_k = (\text{IP} + E_{\text{MO}})$  is taken as a measure of violation of the Koopmans' theorem. We will apply this notion to the calculations by the density functional method. Figure 5 shows the Koopmans' defect for the molecular orbitals of complexes **I–III** and C<sub>4</sub>H<sub>6</sub>Fe(CO)<sub>3</sub> obtained from the calculations by the restricted Hartree–Fock method (RHF/6-31G\*) and the density functional method (B3LYP/6-31G\*). The line passing through the zero of the energy scale corresponds to exact fulfillment of the Koopmans' theorem. In the case of the calculations by the Hartree–Fock method, a large negative deviation from the Koopmans' theorem is observed for the  $3d$  molecular orbitals ( $\Delta_k(3d) = -4.59 \pm 0.55$  eV), while, for the  $\pi$  molecular orbitals, the Koopmans' theorem is fairly well satisfied ( $\Delta_k(\pi) = -0.02 \pm 0.59$  eV). In the calculations by the density functional method, the deviation from the Koopmans' theorem is constant and positive for both the  $3d$  orbitals ( $\Delta_k(3d) = 1.53 \pm 0.18$  eV) and the  $\pi$  orbitals ( $\Delta_k(\pi) = 2.04 \pm 0.19$  eV).

It is obvious that, for both the Hartree–Fock and the density functional methods, the value of the Koopmans' defect depends on the degree of localization of the molecular orbitals. In the case of the calculations by the density functional method, a slight sag of the curve describing the Koopmans' defect (Fig. 5) is possibly





**Fig. 5.** Koopmans' defects  $\Delta_k$  calculated by the density functional (B3LYP/6-31G\*) and restricted Hartree-Fock (RHF/6-31G\*) methods for the (●)  $\pi$  MOs (DFT), (○)  $3d$  MOs (DFT), (▲)  $\pi$  MOs (RHF), and (△)  $3d$  MOs (RHF) of complexes **I–III** and  $C_4H_6Fe(CO)_3$ .

related to the fact that the hybrid B3LYP potential [32, 33] includes 20% of the Hartree-Fock exchange potential. Therefore, a further improvement of the exchange-correlation Kohn-Sham potential may lead to a better agreement with experiment.

Therefore, indeed, in the class of the  $\eta^4$  irontricarbonyl complexes under study, the Kohn-Sham orbital energies can be considered as approximate vertical ionization potentials,

$$\varepsilon_{KS}(3d) = -IP + 1.53(\pm 0.18) \text{ eV}, \quad (2)$$

$$\varepsilon_{KS}(\pi) = -IP + 2.04(\pm 0.19) \text{ eV}, \quad (3)$$

with some energy correction, which depends on the degree of localization of the electron density of the one-electron MOs. In our opinion, this important inference casts desired light on the understanding of the physical meaning of the Kohn-Sham orbital energies.

## CONCLUSIONS

In this study, we showed that the quantum-chemical calculations of the ground state of  $\pi$  complexes of iron **I–III** performed in terms of the restricted method of the density functional theory with the hybrid exchange-correlation potential B3LYP in the 6-31G\* basis set not only reproduce well the geometrical parameters of these molecules, but also describe correctly the sequence of their excited ionic states in a wide energy range (7–12 eV). Our study supports the modern theoretical notion that the Kohn-Sham orbital energies can be considered as approximate vertical ionization potentials. This opens a wide range of possibilities for interpretation of the photoelectron spectra of complex organometallic systems.

On the basis of quantum-chemical calculations by the density functional method, the HeI and NeI photoelectron spectra of irontricarbonyl complexes of  $\alpha$ -

methylstyrene, orthoquinodimethane, and cyclooctatetraene were interpreted. The ratios of the photoionization cross sections  $\sigma_\pi/\sigma_{3d}$  of these molecules were estimated through the relative areas of the  $\pi$  and  $3d$  bands.

The analysis of the spectral and calculation data allows us to conclude that the characteristic feature of formation of chemical bonds in complexes **I–III** is the population and significant stabilization of the antibonding LUMO of a ligand, which leads to a partial aromatization of the bonds of the  $\eta^4$  fragment and to formation of a diene structure from the remaining part of the organic ligand. Furthermore, it was ascertained that the metal  $3d$  MOs are grouped in a narrow energy range, which is typical for other  $\pi$  complexes of transition metals, i.e., ferrocene or irontricarbonyl complexes. The predominance of reverse donating over direct donating in the complexes under study leads to the occurrence of a negative charge on an organic ligand, which is mostly concentrated on the terminal carbon atoms of the  $\eta^4$  fragment rather than distributed uniformly over the entire ligand. The bonding energies of the L-Fe(CO)<sub>3</sub> bonds of complexes **I–III** were estimated.

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