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Abstract

Full Text

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ON SOME RESULTS OF AN X-RAY SPECTRAL STUDY OF FERROCENE AND ITS DERIVATIVES

(Presented by Academician A. P. Vinogradov on 16 XI 1960)

Recently E. M. Shustorovich and M. E. Dyatkina ($^{1-3}$) calculated the molecular orbitals and the distribution of electronic charge in molecules of a series of aromatic complexes. It was of interest to test some of the conclusions of the theory by studying the fine structure of the X-ray absorption spectra of the metal in these compounds. The fundamental possibility of such use of X-ray spectral data, indicated as early as in (^{4}), has become practically feasible in recent years as a result of improvements in the theory of X-ray spectra and the development of methods for calculating their fine structure ($^{5-9}$).

Experimental data on the X-ray absorption spectra of transition metals in many bis-cyclopentadienyl compounds were obtained mainly in ($^{10-13}$). In 1958 the fine structure of the iron K-absorption spectra in $Fe(C_5H_5)_2$ and $Fe(C_5H_5)_2Cl$ was also studied in our laboratory*. These data formed the basis for our further theoretical investigations. For comparison, under the same conditions, X-ray K-absorption spectra of iron were obtained in potassium ferro- and ferricyanides, as well as in $FeSO_4 \cdot 7H_2O$ and $Fe(NO_3)_3$. The relative position of the principal maximum of the X-ray K-absorption spectra of iron in the compounds studied is illustrated by the figures given in Table 1. As is evident, the results of our measurements for the first four compounds agree well with the literature data (^{14}). The spectra were studied with a focusing reflection X-ray spectrograph and were recorded photographically with the rays incident perpendicularly on the film. The reflecting crystal was quartz, planes $(13\bar{4}0)$. The comparison lines were Co $K\alpha_{1,2}$. Exposure was 3-6 hours. Operating conditions were 15 kV and 50 mA. Effective absorber thickness was 5 mg/cm^2.

Fig. 1. X-ray K-absorption spectra of iron in $Fe(C_5H_5)_2$ (1) and $Fe(C_5H_5)_2Cl$ (2).

Table 2

Compound	$FeSO_4 \cdot 7H_2O$	$K_4[Fe(CN)_6]$	$K_3[Fe(CN)_6]$	$Fe(NO_3)_3$	$Fe(C_5H_5)_2$	$Fe(C_5H_5)_2Cl$
Energy, eV	0	1.9	3.8	6.8	6.1	6.1

In Fig. 1 the X-ray K-absorption spectra of iron in $Fe(C_5H_5)_2$ and $Fe(C_5H_5)_2Cl$ are compared after correction for instrumental distortions—

* The work was reported at the All-Union Conference on X-ray Spectroscopy in Rostov-on-Don on June 30, 1959.

tions. Here the abscissa axis gives the energies of the X-ray quanta, reckoned from an arbitrary zero, and the ordinate axis gives quantities proportional to the absorption coefficient. As can be seen, the structure of the iron K-absorption edges in the two compounds is in many respects analogous, and the spectra differ only in the course of the change in the absorption coefficient in the longest-wavelength region of the edge.

In calculating the experimental iron absorption edges in the complexes under consideration, we proceeded from the repeatedly proven (^{6,15,16}) assumption of the hydrogen-like character of the system in which, in gaseous molecules or crystalline complexes with an approximately central symmetry of the field, an electron torn from the K-shell moves outside the filled shells of the absorbing atom. In this approximation, the system of selective absorption lines and the continuous edge (which together form the fine structure of the main K-absorption edge of the element in the compound) can be calculated by means of the relations

$$\varepsilon_n = \varepsilon_\infty - \frac{\eta^2}{n^2}\mathrm{Ry}; \tag{1}$$

$$\frac{\tau_n}{\tau_\infty} = \frac{4\eta^2}{\pi\Gamma}\frac{n^2-1}{n^5}, \tag{2}$$

in which ε_n and ε_∞ are, respectively, the energies of transition of the K-electron to one of the np-levels of the system and to the boundary of the continuous spectrum; τ_n is the height of the n-th absorption line; τ_∞ is the height of the continuous spectrum; Γ is the width of the absorption lines and of the boundary of the continuous spectrum; Ry is the Rydberg constant; n is the effective principal quantum number of the n-level of energy; and η is the effective charge of the K-ionized absorbing atom in the molecule. The last of these formulas was recently obtained in (^{9}) as the result of a derivation more rigorous than that given in (^{7}), and, as verification has shown (^{17}), it works well in calculating the spectra of many molecules in which central symmetry of the field is preserved. However, an attempt at direct application of relation (2) for calculating the K-absorption edge of a metal atom in molecules of the ferrocene type encounters certain difficulties, since the ratio τ_n/τ_∞ obtained from experiment proves to be substantially greater than the value following from formula (2) when (1) is taken into account. Within the framework of the one-electron approximation, it seemed natural to explain this fact by the influence of the electric field of the molecule (which in the present case has D_{5d} symmetry) on the hydrogen-like system formed after K-ionization of the central atom.

Table 2

Characters of the irreducible representations of the group D_{5d}

	E	$C_5^{\pm 1}$	$C_5^{\pm 2}$	$5u_2$	I	$S_{10}^{\pm 1}$	$S_{10}^{\pm 3}$	$5\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	1	1	1	-1
E_{1g}	2	$2\cos\frac{2\pi}{5}$	$2\cos\frac{4\pi}{5}$	0	2	$2\cos\frac{2\pi}{5}$	$2\cos\frac{4\pi}{5}$	0
E_{2g}	2	$2\cos\frac{4\pi}{5}$	$2\cos\frac{2\pi}{5}$	0	2	$2\cos\frac{4\pi}{5}$	$2\cos\frac{2\pi}{5}$	0
A_{1u}	1	1	1	1	-1	-1	-1	-1
A_{2u}	1	1	1	1	-1	-1	-1	1
E_{1u}	2	$2\cos\frac{2\pi}{5}$	$2\cos\frac{4\pi}{5}$	0	-2	$-2\cos\frac{2\pi}{5}$	$-2\cos\frac{4\pi}{5}$	0
E_{2u}	2	$2\cos\frac{4\pi}{5}$	$2\cos\frac{2\pi}{5}$	0	-2	$-4\cos\frac{4\pi}{5}$	$-2\cos\frac{2\pi}{5}$	0

The characters of all irreducible representations of the group D_{5d} are given in Table 2. As is seen, the odd representations of this group are realized by transformation of a six-dimensional basis. This means that, in a field of the symmetry under consideration, there is a sixfold increase in the number of states into which the $1s$-electron knocked out in the process of K-absorption can be captured, as compared with the three p-states of a hydrogen-like system in fields of other symmetry or in the absence of an external field.

If the separation between these levels is small (in comparison with the width of the K-state of the absorbing atom), then, owing to this, one may expect a twofold increase in the relative intensity of the selective x-ray absorption lines of the central atom in molecules of the type under consideration, as compared with those molecules in whose field the above-mentioned "multiplication" of levels does not occur. As the degree of ionicity of the bonding forces in molecules of the type $\mathrm{Me(C_5H_5)_2}$ increases, and as the field strength acting on the central atom increases, the separation between the energy levels that capture the $1s$-electron in the process of K-absorption should increase; along with this, the width of the selective absorption bands should increase. Conversely, the intensities of these bands should then decrease, and, for example, for such practically ionic compounds as $\mathrm{Mn(C_5H_5)_2}$, it should already differ insignificantly from the value calculated by formula (2). Analysis of all the experimental material presently available confirms the validity of these conclusions. Therefore, in calculating the fine structure of the absorption spectra of the metal in bis-cyclopentadienyl complexes with typically covalent bonds (such, for example, as ferrocene), we assumed that the increase in the relative intensity of the selective absorption lines is close to the maximum*. In this case, the calculation of the spectrum and the determination of the energy constants relating to the absorbing atom in such molecules can be carried out without particular difficulty. Figures 2 and 3 present the results of a calculation, performed in this way, of the x-ray K-absorption spectrum of iron in the molecules $Fe(C_5H_5)_2$** and $Fe(C_5H_5)_2Cl$. As is seen, they are in good agreement with the data obtained theoretically $(1, 3)$.

Fig. 2. Calculation of the fine structure of the x-ray K-absorption spectrum of iron in $Fe(C_5H_5)_2$. The heavy line is the experimental curve; the thin lines are the lines of selective absorption and the continuous edge; the hatched absorption band is associated with transitions of 1s-electrons to molecular energy levels; the dots mark the total theoretical absorption curve due to absorption of the "exciton" type.

The magnitudes of the charges concentrated on the iron atoms in both complexes studied proved to be practically (within the accuracy of their determination—division from X-ray spectra coinciding with one another and close to +0.7, while the two other parameters characterizing the state of the absorbing atom in the compound are $n = 1.75$, $\Gamma = 11.2$ eV. This means that, for example, in comparison with the X-ray spectrum of iron in $K_3Fe(CN)_6$ ($\eta' = \eta - 1 = 1$; $n = 1.7$ and $\Gamma = 7.5$ eV), in the spectra of ferrocene the most substantial changes are undergone by the width of the selective absorption bands, which increases by almost 50% owing to broadening of the final level of the photoelectron transition in the molecule. As was to be expected on the basis of theoretical calculations, in the X-ray absorption spectra of the metal in aromatic complexes, along with a series of absorption bands of the "exciton" type, there is also observed a fairly intense band, whose appearance is due to transitions of the 1s electrons of the absorbing atom to a group of molecular levels of the corresponding symmetry. The width of these bands agrees well with what may be expected on the basis of analysis of data (1) on the energies of the corresponding molecular orbitals of the complexes, while their relative intensity changes on going from the spectrum of iron in ferrocene to the spectrum belonging to the cation. In ferricinium it is

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* To estimate the error that may be introduced into the results of the calculation owing to an insufficiently exact value of the correction coefficient in formula (2), we note that a deviation of this quantity from the value chosen by us (two) by 50% may, other conditions being equal, lead to an increase in the calculated charge on the iron atom in the ferrocene molecule by only 15%.

** At the time this work was being prepared for press, a paper appeared (18) in which a similar attempt was made to calculate the x-ray K-absorption edge of iron in ferrocene, obtained in work (13). As verification showed, this calculation is erroneous.

5% greater than the intensity of the molecular band in the spectrum of iron in the neutral molecule.

Fig. 3. Calculation of the fine structure of the X-ray K-spectrum of absorption of iron in $Fe(C_5H_5)_2Cl$. The designations are the same as in Fig. 2.

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